SPECTRALLY RESOLVED THERMOLUMINESCENCE MEASUREMENTS IN POLY(N-VINYLCARBAZOLE) BLENDS

E. Mandowska, A. Mandowski, S. Tkaczyk, J. Swiatek

Institute of Physics, Pedagogical University,
ul. Armii Krajowej 13/15, 42-200 Częstochowa, Poland,

INTRODUCTION

The first scientifically recorded observation of thermoluminescence (TL) was made in 1663 by Robert Boyle who noted a 'glimmering light' from a hot diamond. It is difficult to pinpoint exactly when the word thermoluminescence was first used in the published literature, but it is certainly used in 1895 by Widemann & Schmidt (1895).

Thermoluminescence is the emission of light from insulators or semiconductor when it is heated. This is not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. TL is the thermally stimulated emission of light following the previous absorption of energy from radiation. The material has to be re-exposed to radiation, where upon raising the temperature will once again produce light emission. TL is merely one of a large family of luminescence phenomena. The various luminescence phenomena are given names which reflect the type of radiation used to excite the emission. Thus we have photoluminescence (with excitation done by optical or ultra-violet light), radioluminescence (nuclear radiations), cathodoluminescence (electron beam), chemiluminescence (generated by chemical energy), triboluminescence (mechanical energy), electroluminescence (electrical energy), bioluminescence (biochemical energy), sonoluminescence (sound waves).

The emission of light takes place a characteristic time τ after the absorption of the radiation and this parameter allows us to sub classify the process of luminescence. We can distinguish between fluorescence in which $\tau<10^{-8}$s and phosphorescence in which $\tau>10^{-8}$s (Garlick, 1949: Curie, 1960). Fluorescence is essentially independent of temperature, whereas the decay of phosphoresce exhibits strong temperature dependence. TL is a kind of phosphorescence in which minutes$<\tau<4.6\times10^{9}$ years (i.e. the age of solar system).

It has already been noted that the temperature at which the TL peak maximum occurs is related to the electron trap depth. This was recognised by Urbach (1930) as the key to the use of thermoluminescence to study trap depth distribution. Randall & Wilkins (1945) formalised the theory of TL by considering the first-order mechanism of electron detrapping. Garlick & Gibson (1948) followed this by considering the second-order case. Using equations for the shape of a first-order or second-order the thermoluminescence glow peak it is possible to calculate trapping parameters E (trap activation energy) and s (so-called frequency factor) from an experimental glow curve. TL is relatively simple technique for obtaining information on energy trap distributions. A simple TL glow curve (TL versus temperature) does not always yield unambiguous information, for instance, when the emission spectrum changes with temperature during a TL measurement. This may be due to the radiative recombination of the released charge occurring at more than one defect site within the crystal. For this reason it is important to be able to obtain 3-D glow curves (emission spectra in which the intensity is displayed as a function of both temperature and wavelength. 3-D glow curves thus give information both about the trap distribution (TL versus temperature) and the charge recombination centres (TL versus wavelength).

In this paper we present some results of the measurements performed in Poly (N-vinylcarbazole) (PVK) blends. The results were obtained by the application of spectrally resolved thermoluminescence and phosphorescence decay.

EXPERIMENT

The PVK (trade name Luvican, provided by BASF) was purified by dissolving in chloroform and re-precipitating it in methanol six times. The powder was then re-dissolved in dioxane or chlorobenzene and layers 50-100μm thick were cast onto thick (0.3mm) cooper disk with diameter of 20mm. The samples were dried in room temperature for 24 hours surrounding by vapour of the dissolvent.

λ T

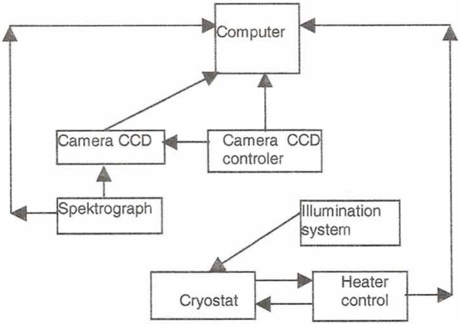

Fig.1. Schematic diagram of apparatus for recording spectrally resolved TL

The TL measurements were carried out in cryostat that enables sample temperature to be controlled between 78K and 700K. Cooling of the sample is carried out using liquid nitrogen. Pressure in the sample chamber is less than 10^{-5} torr.

The linear temperature rise with respect to time is driven by the Autotuning Temperature Controller. The samples were excited with 75 watt Xenon arc lamp installed in a high intensity illumination system. The luminescent intensity was monitored using the spectrograph connected with the LN/CCD-1024E camera (chip format 1024x256, spectral range: 190nm-1080nm). The CCD camera is liquid nitrogen-cooled. It is connected with the temperature controller, which is necessary to stabilise the temperature work of the camera (-70°C—130°C). Temperature-resolved TL signals can be obtained using specialised software. Schematic diagram of this arrangement is shown in fig.1. The sample was cooled down to 87K and then was excited by UV light (for example 325 nm or 365 nm). The TL intensity was monitored when the sample was heated from 87K to 300K at a constant heating rate of 0.8K/s.

RESULTS

Thermoluminescence (TL) in PVK blends re-dissolving in chlorobenzene is presented fig. 2 and fig. 3. Information about excitation and spectral response is included in table 1. During excitation at 365nm of PVK in chlorobenzene apart from the main peak at 580nm (which was also observed during excitation at 325nm) we measured a peak at 410nm. TL in PVK is dependent of excitation wavelength. Mainly peaks appear in the temperature range 110K..120K.

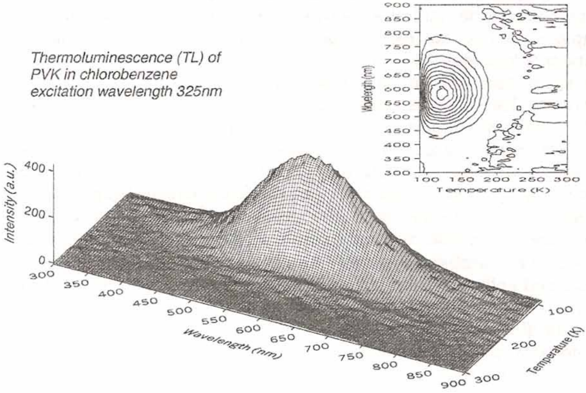

Fig. 2. Thermoluminescence (TL) of PVK in chlorobenzene; excitation wavelength 325 nm. Maximum intensity is detected for 580 nm

Table 1. Thermoluminescence (TL) of PVK re-dissolved in chlorobenzene λ_{ex} - excitation wavelength, t_{ex} - excitation time, $\Delta\lambda$ - spectral range of TL, λ_{max} - maximum intensity wavelength of the peak (I_{max}), ΔT - temperature range of the measurement, T_{max} - temperature range in which was observed maximum intensity of the peak

λ_{ex}(nm)	t_{ex}(min)	$\Delta\lambda$(nm)	ΔT(K)	T_{max}(K)	λ_{max}(nm)	I_{max}(a.u.)
325	2	420-800	88-210	113-120	580	526
365	2.5	370-770	91-190	119-123	580 410	649 206

Table 2.Thermoluminescence (TL) of PVK re-dissolved in dioxane

λ_{ex}(nm)	t_{ex}(min)	$\Delta\lambda$(nm)	ΔT(K)	T_{max}(K)	λ_{max}(nm)	I_{max}(a.u.)
325	15	450-780	81-215	113-120	580 530	327 253
365	15	420-800	81-214	112-120	580	390

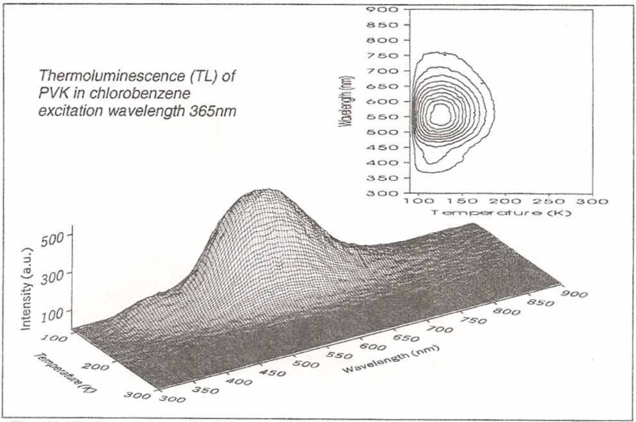

Fig. 3. Thermoluminescence (TL) of PVK in chlorobenzene with excitation done at 365 nm. Maximum intensity is for 580nm. The position of the second peak is 410nm

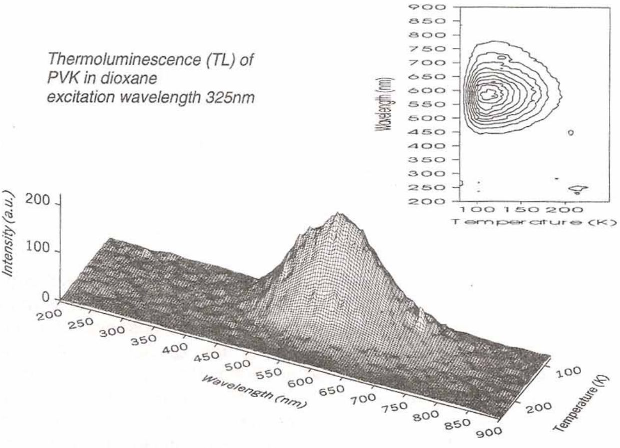

Fig. 4. Thermoluminescence (TL) of PVK in dioxane after excitation at 325 nm. Maximum intensity is observed at 580 nm

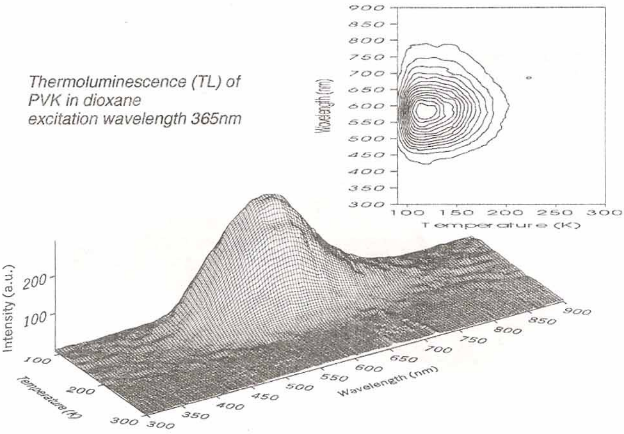

Fig. 5. Thermoluminescence (TL) of PVK in dioxane after excitation at 365nm. Maximum intensity is observed for 580nm

Thermoluminescence (TL) in PVK blends re-dissolving in dioxane is presented in fig. 4 and fig. 5. The information about excitation and spectral response is included in table 2. The main peak is observed for 580 nm when the sample was excited with wavelengths 325 nm and 365 nm. After 325 nm excitation an additional peak was observed with the maximum at 530nm. Essentially, the peaks also appear within the temperature range 110K..120K

CONCLUSIONS

The maximum intensity of TL for all samples was observed within the temperature range: 110K...120K. The maximum intensity of TL is at the wavelength of 580nm. Additional TL peak could be observed at 410nm (for PVK re-dissolved in chlorobenzene for λ_{ex}=365nm). Also, an additional peak could be observed at 530nm (for PVK re-dissolved in dioxane for λ_{ex}=325nm). It was proved that TL mechanism in PVK blends is dependent on the kind of the solvent and the excitation wavelength. Therefore, in PVK blends there exist at least three different types of long-lived recombination processes.

REFERENCES

Becker, K. (1973). *Solid state dosimetry.* CRC Press, Cleveland.
Boyle, R. (1663). *Register of the Roy. Soc.*, 1663, 213.
Cameron, J.R. Suntharalingman, N. & Kenney, G.N. (1968). *Thermoluminescence dosimetry.* Univ. Wisconsin Press, Madison.
Cooke, D.W., Rhodes, J.F., Santi, R.S. & Alexander, C. (1980). J. Chem. Phys., 73, 3573.
Curie, D. (1960). *Luminescence in crystals.* Methuen, London
Garlick, G.F.J. (1964). *Nature*, 202, 171.
Garlick, G.F.J. & Gibson, A.F. (1948*). Proc. Phys. Soc.*, 60, 574.
Kriegseis, W. & Scharmann, A. (1980). Nucl. Instrum. Meth., 175, 239.
McKeever, S.W.S. (1985). *Thermoluminescence of Solids.* Cambridge University Press, Cambridge.
Randall, J.T. & Wilkins, M.H.F. (1945a). *Proc. Roy. Soc. Lond.*, 184, 366
Randall, J.T. & Wilkins, M.H.F. (1945b). *Proc. Roy. Soc. Lond.*, 184, 390
Townsend, P.D. & Kelly, J.C. (1973). Colour centers and imperfections in insulators and semiconductors. Sussex University Press, London.
Urbach, F. (1930). *Wiener Ber.*, 139, 363
Widemann, E. & Schmidt, G.C. (1895). *Ann.Phys. Chem. Neue Folge*, 54, 604.