Polymer Bulletin 8, 211-217 (1982)

**Polymer Bulletin**

# Analysis of Thermoluminescence Curves of Polymers Using Current Methods of Relaxation Phenomenology

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## Summary

It is demonstrated that, for the $\gamma$ relaxation in polystyrene, an adequate description of thermoluminescence curves for several temperature-time programs is possible using only properties of the polymer relaxation process. A distribution function depending only on one variable, the material time, is introduced. Possible modifications at the glass transition are suggested. The new method is compared with the traditional analysis.

## Introduction

The original analysis of the thermoluminescence (TL) process is due to RANDALL and WILKINS (1945). These authors used the equation

$$I \sim - dn/dt = n\ S\ \exp\ (-E/kT)$$

where I is the total luminescence intensity, dn/dt is the time rate of change of the concentration of trapped electrons, S is the attempt-to-escape frequency factor for an electron in a trap with activation energy E, k is Boltzmann's constant, and T is the temperature. This equation has been generalized many times, see e.g. CHEN (1976) for a review. The introduction of trap distributions with respect to E, or E and S, was an important step in this field.

If the movement of electrons from the traps to the TL centres in amorphous polymers is mediated by such molecular mobilities which are responsible for a secondary relaxation or a glass transition, then, of course, the properties of the TL curves are related to the properties of these relaxations. (PARTRIDGE 1965). Very broad distributions of relaxation times (from three to six logarithmic decades, say) are typical for both secondary relaxations and glass transitions. Now, a distribution of relaxation times is certainly not quite the same as a distribution of trap parameters. If the influence of the relaxation is great enough, then its very broad distribution can cover all details of any elementary process such as first or second-order kinetics, parameters of the detrapping process, and the kinetics of a single transport step (hopping). The difference between no, single, or repeated retrapping, and between short or long diffusion paths, can also be hid.

0170-0839/82/0008/0211/$01.40

In this work, therefore, an extremely alternative approach is suggested. It is assumed that only the properties of the relaxations (and not of the traps) are needed for a description of TL curves in amorphous polymers. The principle of time temperature equivalence (a fundamental feature of relaxations in polymers and other glasses) implies that the wanted distribution function depends, approximately, only on one variable, the material time (HOPKINS 1958, MORLAND and LEE 1960). Formulas are obtained which describe TL curves for an arbitrary temperature-time program after and before excitation. Some experimental results of PENDER and FLEMING (1977) for the $\gamma$ relaxation in polystyrene (PS) can be reproduced. It is demonstrated for this relaxation that an isothermal decay curve and a TL curve for a quenching cycle can be predicted adequately from only one glow curve at a constant heating rate.

## Secondary relaxations

The material (also reduced or effective) time $\zeta$ is defined as

$$\zeta = \zeta(t;T(t')) = \int^{t} dt'/a_{T(t')} \approx \text{const} \int^{t} dt'/\tau(T(t')) \qquad (1)$$

where $a_T$ is the shift factor of the relaxation, $T(t')$ is the temperature-time program on the past, $t' < t$, and $t$ is the actual time. Roughly spoken, $\zeta$ measures the time in units of a mean relaxation time $\tau(T)$. A distribution (or spectrum) $\phi$, $0 \leq \phi \leq 1$, is defined as that part of TL active electrons which caused a TL signal in the past. Clearly, the relation to the TL intensity is given by

$$I = \text{const}\ d\phi/dt \ . \qquad (2)$$

Provided that those characteristics of TL which are not directly determined by the polymer mobility (such as the quantum yield) have only a negligible dependence on temperature and/or time, then $\phi = \phi(\zeta)$. I should underline again that $\phi$ is considered as a representative for the molecular mobility in a relaxation zone of a polymer and not as a distribution of trap parameters.

The temperature dependence of a characteristic frequency $\nu$ of a secondary relaxation can usually be described by an Arrhenius equation,

$$\ln \nu = \ln \Omega_A - A/T \ , \qquad (3)$$

where $\Omega_A \approx 10^{13}$ Hz, $A/T_o = \ln(\Omega_A/\nu_o)$, and $(T_o, \nu_o)$ is a fixed reference point $\nu = \nu_o$ in an Arrhenius plot. The shift factor is defined as $a_T = \nu_o/\nu$ .

Two interpretations of the distribution $\phi(\zeta)$ are possible: (i) For a given scale of time, $1/\nu_{eff}$, (e.g. for a given heating rate $\dot{T}$ at constant pressure), $\zeta$ depends only on the temperature T. This means $\phi$ is only a function of T, too. Consider* the secondary relaxation zone as an ensemble of local molecular motions having a distribution of energy barriers, $E_A$, then T can be transformed into $E_A$ by

$$E_A = kT \ln(\Omega_A/\nu_{eff}). \qquad (4)$$

Therefore we obtain $\phi$ as a function of $E_A$. Remember that $E_A$ (activation energy of a secondary relaxation) is, in principle,

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* *Considering*

different from E (activation energy of the primary traps, for instances).
(ii) In the case T=const, $\zeta$ is controlled only by the relaxation time $\tau$ and we obtain $\phi$ as a function of $\tau$. Practically, plotting $\phi$ as a function of $\ln\zeta$ , $\phi$ is to be the same function of $\ln\tau$ when one point on the $\ln\zeta$ -axis is gauged anew by $\ln\tau$ with the aid of eq.(1).

Thus $\phi$ can be conceived either as distribution of activation energies, $E_A$, or of relaxation times, $\tau$ ; both $E_A$ and $\tau$ characterizing the relaxation zone of the polymer.

Analysis of TL curves for PS

PENDER and FLEMING (1977) measured TL glow curves, quenching cycles, and isothermal decay curves for the $\gamma$ relaxation in PS. Using only their glow curve for the 310 nm band, I calculated $d\phi/d\ln\zeta$ as a function of $\ln\zeta$ , $d\phi/dE_A$ as a function of $E_A$, the isothermal decay I(t) for T = 122.8 K, and the first quenching cycle for this band.

The material time is obtained from eqs.(1) and (3) as

$$\zeta = \int_{t^o}^{t} dt' \exp\left\{A\left[T(t') - T^o\right]/T(t')T^o\right\}, \qquad (5)$$

where $(T^o,\ t^o)$ is the start point of the experiment after irradiation (at about 80 K). The slope A = 1990 K was obtained using a reference point $(\nu_o, T_o)$ = (1Hz, 153 K) from mechanical measurements.

Transforming eq.(2) into $I(T) = \mathrm{const}(d\phi/d\ln\zeta)(d\ln\zeta/dt)$, the distribution $d\phi/d\ln\zeta$ can be calculated from the glow curve I(T) at a constant heating rate ($d\ln\zeta/dt$ is obtained from eq.(5)).

The activation energy distribution $d\phi/dE_A$ is obtained directly from the glow curve when the T-axis is gauged in $E_A$ with the aid of eq.(4). The effective frequency can be estimated from the heating rate $\dot{T}$ as $\nu_{eff} = \dot{T}/\Delta T$. I used $\Delta T$ = 5K, $\dot{T}$ = 0.067 K/s was given by the experimentators, which yields $\nu_{eff} \approx 13$ m Hz.

Both distributions are shown in Fig.1

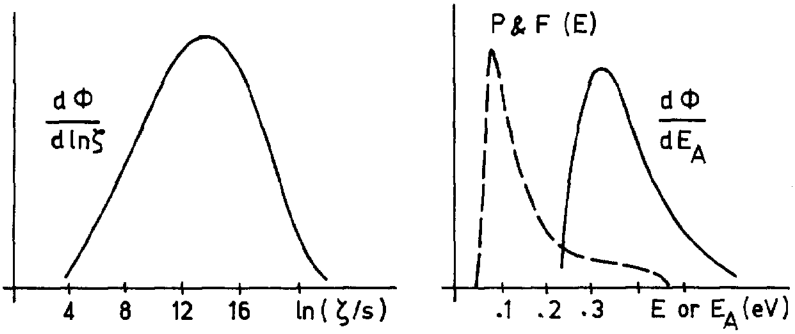

Fig.1 Nonnormalized TL relaxation spectra for the $\gamma$ relaxation in PS (310 nm band) as a function of material time $\zeta$ (on the left) and of activation energy $E_A$

Since the relation between $\ln \zeta$ and T is not linear, $d\phi/d\ln\zeta$ has an other shape as the glow curve. $d\phi/d\ln\zeta$ can also be considered as a distribution of relaxation times as explained above. The other distribution, $d\phi/dE_A$, is compared to the activation energy distribution of occupied electron traps at 80 K as calculated by PENDER and FLEMING (1977), their $n_0(E)$ is labelled as P & F(E) in Fig.1. I think the peak at 0.08 eV is an overstimate resulting from their adjustment with two functions, $n_0(E)$ and $S(T)$, in the frame of trap parameters. If all details of trap kinetics are assumed to be covered by the very broad relaxation spectrum $\phi$, such functions would be unappropriated for an adjustment, and it would be not probable that one can obtain trap distributions from TL curves in polymers.

Integrating $d\phi/d\ln\zeta$ gives $\phi(\zeta)$. The intensity $I(t)$ for any temperature-time program $T(t')$ can now be calculated from eqs.(2) and (5). The result for the isothermal decay at T=122.8 K is compared with the experimental findings (P&F) in Fig.2.

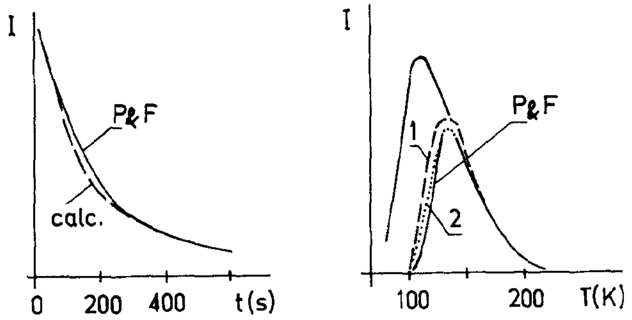

Fig.2 TL intensity I for the isothermal decay at T=122.8 K (on the left) and the first quenching cycle for the $\gamma$ relaxation in PS (on the right, the original glow curve is also shown here)

Two curves are calculated for the first quenching cycle (quench at the maximum temperature of the original glow curve and heating again with the same $\dot{T}$): curve 1 (see Fig.2, on the right) is for quenching immediately after T=122.8 K is reached, and curve 2 is for quenching after a delay of 30 s (which interval was quoted by the experimentators) between reaching 122.8 K and quenching. During this delay, T=const was assumed.The calculated intensity is rather sensitive to such small changes of the temperature-time program as can be seen from the diagram.

Fig.2 shows that a fair agreement between experimental (P&F) and calculated (calc.,1,2) curves can be achieved. No adjustment is necessary if the proportionality constants are handled with care. Knowledge of trap parameters is not necessary. Therefore, a description of TL curves for $\gamma$(PS) seems to be possible using only properties of the polymer relaxation.

## Interpretation of the frequency factor

This section is to show that there is an "intrinsic" frequency factor, s, in our approach, intrinsic with regard to the relaxations, Fig.3 shows how such a factor can be introduced for a glow experiment with a constant heating rate $\dot{T}$.

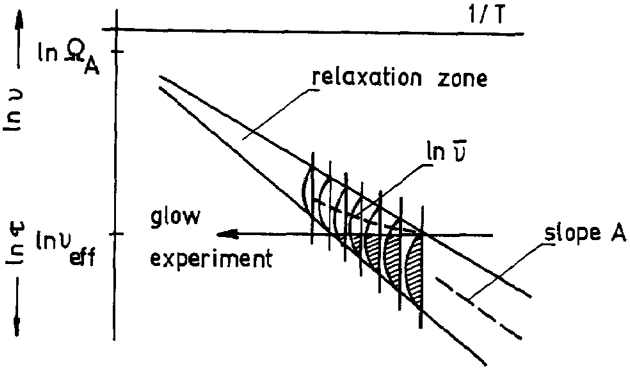

Fig.3 Orign of an intrinsic frequency factor $s=\bar{\nu}/\nu_{eff}$ resulting from a broad distribution of relaxation times

The attemps are counted by a mean frequency $\bar{\nu}$ of the working part (non hatched) of the distribution. "Thawing" of the frozen parts (hatched) allows escaping of electrons which is therefore characterized by the experimental time scale $1/\nu_{eff}$. Obviously, an attempt-to-escape factor with respect to the relaxations can be defined as $s=\bar{\nu}/\nu_{eff}$.

Since $\bar{\nu}$ increases when the temperature is increased, s increases too. But the slope of s, $|d\ln s/d(1/T)|$, is smaller than the mean slope A of the secondary relaxation as can be seen from Fig.3. These properties of s correspond to the findings of PENDER and FLEMING (1977) with regard to their frequency factor of traps, S(T). Probably, there is some projection of the relaxation properties into the frame of trap distributions presumed by these authors.

By the way, a broadening of our distribution function $\phi$ (due to the elevation of pressure, for instances) leads to an increase of our frequency factor s at a given temperature, and to a decrease of its mean slope, if the mean position of the secondary relaxation in an Arrhenius plot is not altered (by the pressure in the example).

## Modifications at the glass transition temperature $T_g$

The material time $\zeta$ near $T_g$ is influenced not only by the actual temperature T (as in the case of secondary relaxations) but also by the fictive temperature $T_f$ according to TOOL (1946)). That is why some modifications of our method are necessary. I suggest, according to a general idea of NARAYANASWAMY (1971) (see DE BOLT et al. (1976), too), that their method stemming from linear response can also be applied for the calculation of $T_f$ with respect to TL. Starting from the general formula of linear response

$$x_B(t) = \int_{-\infty}^{t} \dot{f}(t')J(t-t')dt' \quad , \tag{6}$$

where $x_B$ is an observable, $f$ is the conjugated force, $\dot{f}=df/dt$, and J is the relevant compliance, we have to substitute

$$x_B \longrightarrow T_f,\ \dot{f} \longrightarrow \dot{T},\ J \longrightarrow \tilde{\phi},\ t - t' \longrightarrow \zeta - \zeta'. \tag{7}$$

The relevant pair of conjugated variables is now T and $T_f$, and $\tilde{\phi}$ is a compliance, with respect to TL. According to the fluctuation dissipation theorem, this compliance is related to a correlation function which is tightly connected with our spectrum $\phi(\tau)$. These relationships are discussed with regard to glass transitions by DONTH (1981). Having a logarithmic broad distribution $\phi$ (some logarithmic decades of $\tau$) we can assume $\tilde{\phi} \approx \phi$. Then we obtain, from eqs. (6) and (7),

$$T_f(t) \approx \int_{t^o}^{t} \dot{T}(t')\phi(\zeta - \zeta')dt' . \tag{8}$$

The integration has to start at a time $t^o$ when the sample is in equilibrium, $T(t^o) > T_g$. In this way the cooling history before excitation influences $T_f$, and therefore I(t).

NARAYANASWAMY (1971) suggested also the following mixing rule for T and $T_f$ with respect to their influence on $\zeta$,

$$\zeta - \zeta' = \int_{t'}^{t} dt'' \exp\left\{B\left[x(T(t'')-T_g)+(1-x)(T_f(t'')-T_g)\right]\right\}, \tag{9}$$

where x (mostly between 0.4 and 0.6) is a mixing parameter and B is the slope of the WLF (Williams-Landel-Ferry) equation near $T_g$, $B=(d\ln\nu/dt)_g$, usually in order of 1/K.

Eqs.(8) and (9) represent a nonlinear system for $T_f(t)$ and $\zeta(t)$. $\phi(\zeta-\zeta')$ and x can be obtained from experimental data of TL intensity I(t) using eqs.(2),(8), and (9) in a regression program. Having $\phi$ and x, this intensity can be calculated for any temperature-time program from these equations. A correlation for $\phi$ is recommended for the wanted computer programs.

The following qualitative prediction can be made from these equations: Consider a set of TL glow curves having the same heating rate $\dot{T}$ but different cooling rates $\dot{T}_c$ before the irradiation, ($\dot{T},\dot{T}_c$ = const near $T_g$.) Then the peak of the glow curve near $T_g$ is sharpened and shifted to higher temperatures, and its low temperature tail is shortened, when the cooling rate is decreased. Such an effect is usually called an overheating. A typical order-of-magnitude estimate is: Increase of peak height 10% and shift of the peak maximum temperature +1 K when $\dot{T}_c/T$ is varied from 10 to 0.1.

## Conclusions

As demonstrated for the $\gamma$ relaxation in PS, a description of TL curves is possible using only properties of the relaxation process. Under certain conditions, the TL curves of polymers give mainly information about polymer mobility as relevant to the movement of TL active electrons.

Further work is needed to clarify the precise meaning of the mobility and to fix the conditions of this statement. As I can see, such conditions are $E \lesssim E_A$, great influence of polymer mobility on detrapping, retrapping, and transport of electrons, and a logarithmic broad distribution $\phi$. Then trap parameters and kinetic details of single transport steps can probably not be derived from I(t) curves, because they are totally covered by the very broad distributions of relaxation times which are typical for amorphous bodies. On the contrary, if the relaxation spectra are narrow as in the case of some organic crystals, for instance, then there is some hope to get information about the traps from I(t).

Since the distribution $\phi$ is calculated by means of a method stemming from linear response, $\phi$ can really be compared with spectra analogously obtainable from other measurements (such as calorimetric, mechanical, dielectrical, after reduction to a common frequency or temperature). Such a comparison should give some insight into the transport process responsible for TL.

I suggest that similar methods can be used for the analysis of other thermostimulated experiments in polymers such as TSC (thermostimulated current), TSP (polarization), and so on. It is likely to expect that the $\phi$'s from different methods are similar but not identical, because the underlying molecular mechanisms are not exactly the same for the different phenomena.

## Acknowledgements

This work was done during a stay at the Charles University Prague. I thank Prof. I. Chudaček, head of the Department of Polymer Physics, for introducing me in the field of TL and for his steady interest in this work. Thanks are due to Dr. S. Nešpůrek from the Institute of Macromolecular Chemistry in Prague for a valuable discussion.

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*Received June 21, accepted after revision August 16, 1982*