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Spectroscopy of Thermoactivated Relaxation Processes in Butadiene-Styrene Copolymers in the Elementary Relaxator Approach

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SUMMARY

The thermoactivated relaxation processes resulting in untrapping of the carriers and in recombination luminescence are described by means of the sum of independent elementary relaxators. In order to describe an elementary relaxator distribution function following characteristics were obtained by the fractional glow technique: i) the mean activation energy, ii) the mean frequency factor, iii) the recombination intensity, iv) activation energy spectrum, v) and frequency factor spectrum for butadiene-styrene copolymer. Using the Boltzmann equation unusually large values of frequency factor and activation energy were obtained, giving evidence that molecular motions γ , α exist in some temperature regions and therefore, that another desciption would be necessary.

INTRODUCTION

After a systematic study of the thermoluminescence (TSL) of polymers (FLEMING,1968, KNAPPE et al. 1974, GEORGE and RANDLE,1975, FLEMING et al. 1971, NIKOL'SKII et al. 1970, KRYSZEWSKI et al. 1970, RANICAR and FLEMING,1972, PARTRIDGE, 1972, LINKENS and VANDERSCHUEREN,1977, PENDER and FLEMING, 1977) a theory was proposed to describe TSL in polymers. It is based on the assumption, that low temperature irradiation provides ionisation and that the free electrons are trapped by the macromolecular chains. Subsequent heating releases the electrons by activating intrinsic molecular motions of the macromolecules and these electrons recombine with ions and emit light. The recently developed new approach (TALE,1981) - the modulation thermoactivation spectroscopy - was applied to the investigation, analysis and description of complicated relaxation processes which result in thermostimulated luminescence (POSPÍŠIL and TALE,1981).

Investigation of the relaxation kinetics in most solids is complicated by the co-existence of both spontaneous (temperature-independent) tunneling and thermoactivated processes. Previous standard methods for investigating the kinetics of relaxation processes (isothermal and isochronal decay, thermostimulated phenomena) are based on some a-priori assumptions strongly restricting the analysis. They are e.g. the existence of a single recombination mechanism, the mono- or bimolecular character of the kinetics, a single kind of traps etc.

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Spontaneous relaxation processes including electron tunneling and resonance energy transfer can be characterized by a dispersion of distribution probabilities of elementary events, whereas thermoactivated processes - by continuous distribution of parameters of the activation barrier, i.e. activation energy, E, and frequency factor, s, which is a pre-exponential co-factor in the probability, w, of over-barrier electron transfer

$$(\tau_{E,s})^{-1} = w = s\exp(-E/kT) \tag{1}$$

Description of thermoactivated relaxation processes

Let us assume, that arbitrary relaxation process can be described by the sum of independent "elementary" relaxators. If $M_{E,s}$ is the initial elementary relaxator distribution function and $m_{E,s}$ is the instaneous distribution, then for an arbitrary process kinetics one gets

$$I(t) = \int_0^\infty\int_0^\infty - \frac{dm_{E,s}}{dt}\,dE\,ds \tag{2}$$

where the change of the concentration of elementary relaxators is defined by the traditional rate equation

$$-\frac{dm_{E,s}}{dt} = \frac{m_{E,s}}{\tau_{E,s}} \tag{3}$$

Solving (3) we get

$$I(t) = \int_0^\infty\int_0^\infty M_{E,s}\, i_{E,s}\,dE\,ds \tag{4}$$

where

$$i_{E,s} = s\exp(-E/kT)\exp(-p\,s) \tag{5}$$

and

$$p = \begin{cases} t\exp(-E/kT) & \text{for } dT/dt = 0 \\ \int_0^T \beta^{-1}\exp(-E/kT)\,dT & \text{for } dT/dt = \beta \end{cases} \tag{6}$$

The equations (4) to (6) represent the integral transformation with the known kernel function $i_{E,s}$.

Let us now consider the validity of the elementary relaxator aproximation for different relaxation processes, usually described in terms of rate equations (BRÄUNLICH,1979). In the case of a process, characterized by E=const (one kind of monoenergetic traps) (4) transforms as follows

$$I(t) \sim F(p) = \exp(-E/kT) \int_{0}^{\infty} M_s \; s \; \exp(-p \; s) \; ds \qquad (7)$$

Eq.(7) represents the Laplace transformation, M_s s being the original of F(p) exp(E/kT). It can be shown that for an arbitrary relaxation kinetics there exists M_s s corresponding to a set of rate equations describing such a process, i.e. the solution of the latter satisfies the necessary and sufficient conditions of the existence of the inverse Laplace transformation. In the case of the first order relaxation kinetics, the M_s is represented by a single kind of elementary relaxators, i.e. the process which follows the first order kinetics in this description acts as an elementary relaxation process in terms of which complicated relaxation process have to be decomposed. Each arbitrary order, c, relaxation kinetics in the case E = const can be described by the sum of elementary relaxators, continuously distributed over frequency factors, s . If n_0 is the number or reaction partners of each kind, s_c, V_c -the frequency factor and reaction volume of the process of reaction order c, then

$$M_s = \frac{s^{(2-c)/(c-1)} \exp\left(\frac{1}{n_0^{(c-1)}} \; \frac{s}{(c-1) \, s_c \, V_c^{(c-1)}} \right)}{(c-1)^{c/(c-1)} \; V_c^{c} \; s_c^{1/(c-1)} \; \Gamma(c/(c-1))} \qquad (8)$$

where Γ is the gamma function.

A process, characterized by continuous distribution of activation energies (several kind of traps), can be described by the elementary relaxators even when every kind of traps having an arbitrary order of relaxation kinetics empties independently from each other. It means that the redistribution between different kinds of traps does not affect the concentration change of reaction partners in the temperature region of preferential thermal emptying of the corresponding kind of traps. Such processes are, for example, the retrapping of electrons by the deep traps before their thermoactivated emptying. Therefore most of the complex relaxation process kinetics can be uniquely described by the elementary-relaxator distribution function- (RDF) of activation energies and frequency factors.

Experimental estimation of the RDF

The desired estimate involves: i) the measurement of the relaxation kinetics employing fractional heating regime, ii) an approximation of the measured results in terms of theoretical model of the process(TALE,1981).The fractional glow technique requires the specific heating regime which is monotonous but with imposed small temperature oscillations (GOBRECHT and HOFMANN,1964), This permits, along with the usually obtainable dependence of the recombination luminescence I vs stimulating temperature T, to get also the mean instantenuous activation energy $\langle E(T) \rangle$ (GOBRECHT and HOFMANN,1964).

$$\langle E\rangle = -\left.\frac{d(\ln I)}{d(1/kT)}\right|_{n\,=\,\mathrm{const}} \qquad (9)$$

where n is the momentary concentration of reaction partners. Based on experimental data, the following characteristics of the relaxation process can be also obtained :

i) the mean frequency factor

$$\langle s\rangle\ (T) = \frac{1}{\beta}\left(\frac{E}{kT^2} - \frac{1}{I}\,\frac{dI}{dT}\right)\exp\left(\frac{E}{kT}\right) \qquad (10)$$

ii) the activation energy spectrum

$$H_E = \frac{1}{\beta}\;\frac{I}{d\langle E\rangle/dT} \qquad (11)$$

iii) the frequency factor spectrum

$$H_s = \frac{1}{\beta}\;\frac{I}{d\,\langle s\rangle\,/dT} \qquad (12)$$

Here H_E , H_s characterize the RDF over activation energies and frequency factors, respectively, i.e.

$$H_E \approx \int_0^\infty M_{E,s}\ ds\ , \quad H_s \approx \int_0^\infty M_{E,s}\ dE$$

An analysis indicates that the construction of the RDF based on experimental I(T), $\langle E\rangle$ (T) belongs to the so-called incorrect reverse problems (TALE,1981). The procedure to estimate the $M_{E,s}$ consists in the approximation of the experimental I(T), $\langle E\rangle$ (T) by a theoretical model in order to get the best fit of the $M_{E,s}$ to the experiment. The presented dialoque procedure for this approximation includes calculation of I(T), $\langle E\rangle$ (T), H_E, H_s, for a given $M_{E,s}$ and β , and a futher comparison of the experimental and theoretical dependence of I(T), $\langle E\rangle$ (T) (TALE,1981a,b).

EXPERIMENTAL

The studied material was polybutadiene-styrene (Solprene 1206) (PBS) purified by several dissolution-precipitation cycles. Samples were prepared by casting a solution of PBS in dichlormethane upon a substrate. X-ray irradiation (tungsten anticathode at 35 kV and 5 mA) was performed at liquid nitrogen temperature in an evacuated cryostat. The intensity of luminescence was detected i) during heating the sample at constant heating rate 0.1 Ks^{-1} (after irradiation) and ii) during specific heating regime.

RESULTS AND DISCUSSION

Typical results for the recombination luminescence of PBS are plotted in Fig. 1 and Fig. 2. Glow curve exhibits three maxima known from our earlier thermostimulated luminescence (TSL) measurements (POSPÍŠIL,1981, POSPÍŠIL and CHUDÁČEK, 1982). The study of the glow curve using fractional glow technique (modulation thermoactivation spectroscopy) revealed quasicontinuous distribution of trapping sites in the low temperature maximum TSL having mean activation energies lying between approx. 0.15 and 0.4 eV. Comparison with the theoretical model has shown that δ – TSL maximum is due to the process having continuous distribution in the range of activation energies of elementary relaxators. The increase of the stimulating temperature is accompanied by the increase of the mean activation energy and of the frequency factor in the range $10^{6}\,s^{-1}$ up to $10^{12}\,s^{-1}$. High temperature TSL maxima, γ and α, correspond to the activation energies 0.7 and 0.9 eV, respectively. The corresponding frequency factors are very large $10^{20}\,s^{-1}$ and $10^{21}\,s^{-1}$, respectively. The semiclassical model of the ionization of local states (CURIE,1960) estimates that the frequency factor of the process limited by thermal release of the electron can not be considerably higher than upper frequency of the lattice vibrations ($10^{14}\,s^{-1}$). Hence,

experimental data give evidence that a more complicated mechanism of the recombination process terminating radiative recombination of charge in γ and α temperature regions exists. From previous measurements it results that γ and α maxima of thermoluminescence glow curve are observed in the temperature region where motion of side groups set in (FROIX et al.,1976) and where molecular motions associated with structural transition T_g in PBS appear (HAVRÁNEK, 1980).

Unusually large frequency factor which correspond to unusually large activation energies at corresponding stimulating temperature regions of the process, may be understood if we suppose an exponentially sharp increase of the reaction volume V_c with temperature (RUDLOF et al.,1978). "Normal" values of activation energy and frequency factor are connected with a certain volume, in which elementary acts and radiation recombination of electrons mutually correspond. If this volume exponentially increases with temperature, then for the recombination a supplementary activation energy is needed. We can suppose that the increased molecular motion at glass transition temperature, is due to both thermal activation and thermal expansion, in accordance with the increased volume concept. It has shown that molecular relaxation processes at glass temperature have relaxation times which can not be given by a simple Boltzmann factor (WILLIAMS et al.,1955). Similary, the maxima in TSL curve γ and α can not be described by a simple elementary relaxator process.

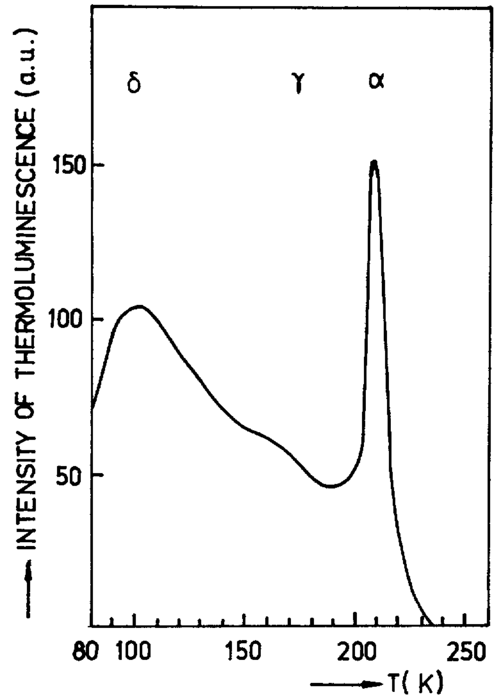

Fig. 1.

Glow curve of PBS (25% bound styrene).

Heating rate 0.1Ks^{-1}

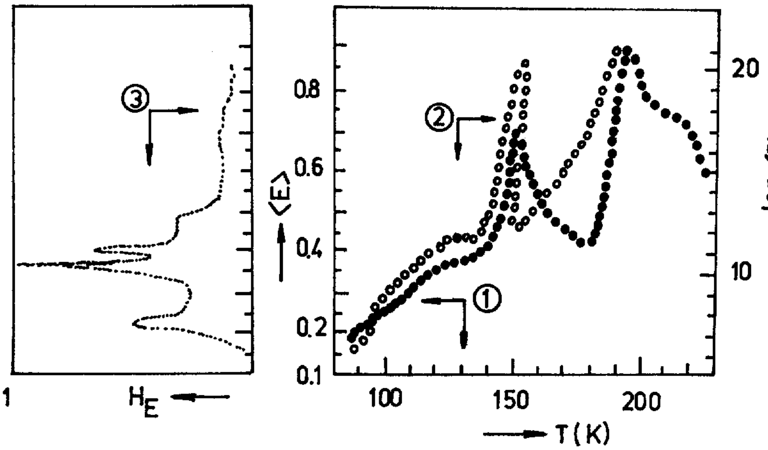

Fig. 2. Temperature dependence of a mean activation energy (curve 1) ,mean frequency factor (curve 2) and the activation energy spectrum (curve 3)

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