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Radiothermoluminescence Curves of Polymeric Materials in the Region of Releasing Frozen Molecular Motions

1. The Shift of Radiothermoluminescence Maxima Resulting from Variation Cooling Rate

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SUMMARY

The glass transition peak of radiothermoluminescence (RTL) curves in a statistical butadiene - styrene copolymer shows a distinct dependence on the cooling rate prior to irradiation. The higher the cooling rate, the lower the intensity and the temperature of the RTL glow curve maximum. These experimental findings are in accordance with a recently proposed theory of RTL in terms of glass transition phenomenology.

INTRODUCTION

After a systematic study of RTL of polymers (FLEMING, 1968, KNAPPE et al. 1974, GEORGE and RANDLE,1975, FLEMING et al. 1971, NIKOL'SKIJ et al. 1970, KRYSZEWSKI et al. 1970, RANICAR and FLEMING, 1972, PARTRIDGE,1972, LINKENS and VANDERSCHUEREN,1977, PENDER and FLEMING,1977) the following theory was proposed: At low temperature, irradiation by X - rays provides ionisation of chromophore groups. The free electrons are trapped by structural or chemical defects of the polymer system. Subsequent heating releases the electrons by activating intrinsic molecular motions of the macromolecules and these electrons recombine with ions of chromophore groups and emit light.

Typical results for low styrene content copolymers are shown in Fig.1 (up to 28 % styrene content by weight). Glow curve exhibits three maxima known from our earlier measurements (POSPÍŠIL, 1981). The study using glow technique - modulation thermoactivation spectroscopy - yielded results with a quasicontinuous distribution of trapping sites in the low temperature RTL (δ- maximum) with mean activation energies lying between 0.15 and 0.4 eV and a frequency factor in the range from $10^{6}s^{-1}$ up to $10^{12}s^{-1}$ (POSPÍŠIL and TALE, 1983). Thermoactivated processes for this case are described by continuous distribution of activation energy , E , and frequency factor , s , (which is a preexponential co - factor in the probability , w , of over-barrier electron transfer)

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

From the high temperature RTL maxima (γ , α) in this description , activation energies 0.7 and 0.9 eV, respectively can be computed. The corresponding frequency factors are very large , $10^{20}s^{-1}$ and $10^{21}s^{-1}$, respectively (Fig.2). These unrealistic values give evidence that a more complicated mechanism of the thermal activation is valid. From previous measurements it follows that γ and α maxima are observed in the temperature region where motions of side groups set in (FROIX et al. 1976) and where molecular motions associated with structural transition T_g appear (POSPÍŠIL, 1981). For the explanation of these values of E and s , the concept of a sharp increase of the reaction volume V_c with temperature (RUDLOF et al.1978) was suggested. An other proposition was utilization of relaxation times given by WLF equation (WILLIAMS et al.1955).

A description of RTL glow curves in terms of contemporary glass transition phenomenology is given by (DONTH, 1982). The basic ideas are from the work of (NARAYANASWAMY , 1971) /cf. also the book of (VAN TURNHOUT , 1974) for a general framework/. The method of linear response is applied to temperature - time programs. The material time ζ dependens not only on the actual temperatur T , but also on the fictive temperature T_f,

$$\zeta - \zeta' = \int_{t'}^{t} dt'' \exp \left\{ B \left[x(T(t'') - T_g) + (1-x)(T_f(t'') - T_g) \right] \right\} \qquad (2)$$

where x is the mixing factor, t is the time and B is slope of the WLF equation near T_g ($B = d\ln\nu / dT\big|_{T_g} \simeq 1/K$).
The fictive temperature is given by

$$T_f(t) \simeq \int_{t_0}^{t} \dot{T}(t')\, \Phi(\zeta - \zeta')\, dt' \qquad (3)$$

Here the integration has to start at a time t_0 when the sample is in equilibrium , $T(t_0) > T_g$. T(t) is the temperature - time program and Φ is the relaxation distribution relevant for RTL

$$0 \leq \Phi \leq 1 \qquad \mathcal{J}_{RTL} \simeq \frac{d\Phi}{dt} \qquad (4)$$

From this theory some predictions followed: (DONTH, 1982). The peak of the glow curve connected with glass transition must shift to the lower temperature region with increase of the cooling rate $|\dot{T}|$. At the same time the maximum intensity of the peak is gradually lowered.

EXPERIMENTAL

We prove to demonstrate these predictions on statistical polybutadiene - styrene copolymer (Krylene 1509) with 23.5 weight % bound styrene content. The sample was purified by several dissolution - precipitation cycles. The excitation of sample with X-rays /tungsten anticathode at 35 kV and 5 mA / was performed at liquid nitrogen temperature in an evacuated cryostat / 10^{-2} Pa/. The sample was heated with rate of 0.1 Ks^{-1}.

Fig.3 shows three RTL glow curves of the same sample which was cooled with three different rates, then identically excited with X-rays and heated with the same rate in all cases. These glow curve have been compared with the results of mechanical relaxations and DTA measurements performed on the same sample made previously (POSPÍŠIL and HAVRÁNEK, 1983). From this follows that the broad γ maximum lying between 140 - 180 K corresponds to the γ relaxation maxima of PBS. This maximum is due to the rotation of phenyl groups (YANO and WADA, 1971). The α maximum corresponds to the glass transition temperature and is the result of cooperative segmental motion of the copolymer main chain. From Fig.3 and Table I we can see, that the temperature position, intensity and half-width of the RTL curve corresponding to this α- maximum exhibit a distinct dependence on the cooling rate prior to excitation.

TABLE I

cooling rate $[Ks^{-1}]$	position of T_α [K]	RTL intensity of T_α maximum [rel. units]	half-width of T_α maximum [K]
0.1	219	184	10
0.2	218.5	130	10
10	215	98	13

The temperature change α- maximum of RTL curve is physically meaningsfull, as it was demonstrated by careful calibration of the Cu - constantan thermocouple used, by measurement of temperature gradient in both longitudinal and transverse directions and by repeating of experiments.

DISCUSSION

The experimental results (Fig.3, Table I) are in accordance with our theoretical predictions obtained for different cooling rates.

We can easily understand the shift of T_{max} to lower, the higher is the temperature cooling rate $\dot{T}_c$: Increasing $|\dot{T}_c|$ is equivalent to higher fictive temperature after freezing (eq.3). According to eq.2 , higher T_f is connected with material time which is measured by "internal"clock , which counts in ζ units. Since Φ is function of ζ only, the maximum of intensity of glow effect is delayed a certain amount of "internal seconds" (ζ units). From that it follows that T_g maximum occurs earlier and because approximation $\dot{T}\,dt = dT$, the maximum of glow curve is located in the low temperature range.

It is not so simple to explain the observed dependence

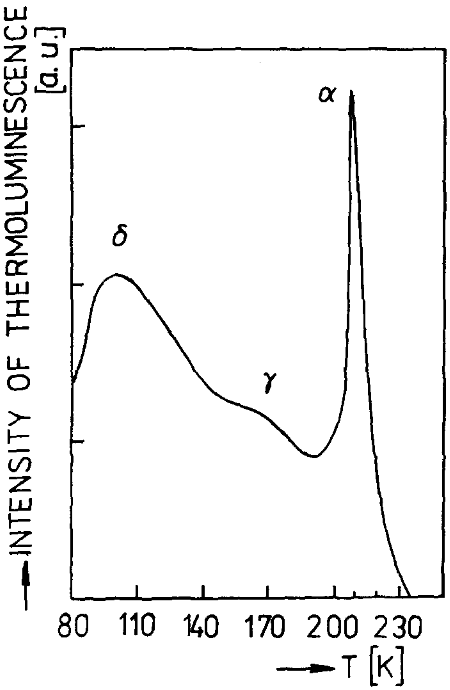

Fig.1
Typical glow curve of PBS (Krylene 1509) with low styrene content (23.5% styrene content by weight)
Heating rate 0.1 Ks^{-1}

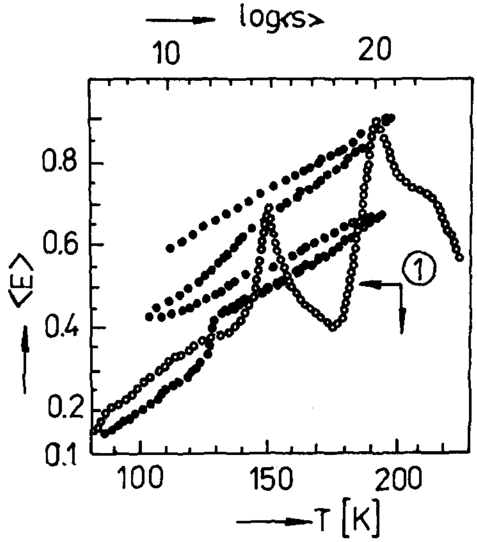

Fig.2
Temperature dependence of the mean activation energy <E> (curve 1) and the mean frequency factor <s>(curve 2) of Krylene 1509

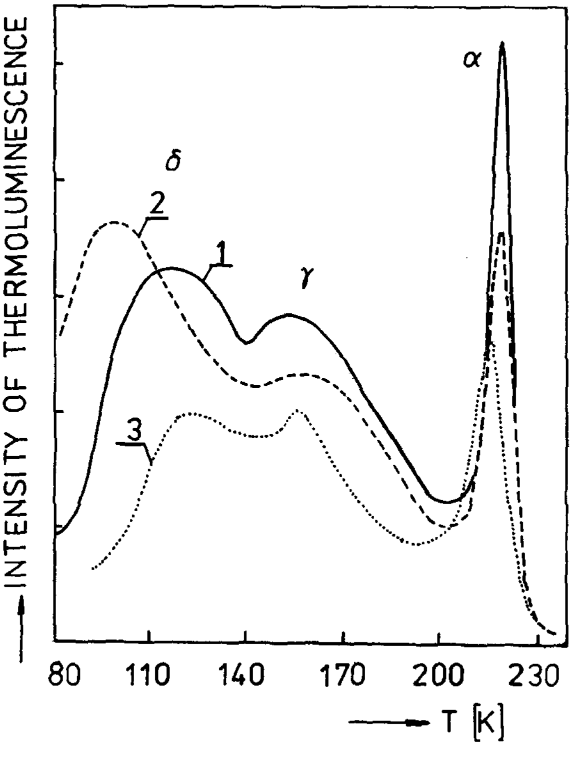

Fig.3
RTL glow curve of PBS (Krylene 1509)
Heating rate 0.1 Ks^{-1}
Cooling rates:
1 ...... 0.1 Ks^{-1}
2 ...... 0.2 Ks^{-1}
3 ...... 10 Ks^{-1}

of the intensity maximum on $|\dot{T}_c|$. Usually the reverse effect, so called overheating effect, is discussed : The lower $|\dot{T}_c|$, the lower T_f at $T < T_g$ and the higher T_{max}. But for non-linearity of eq.2 and 3, there exists a sudden rise of T_f near T_g for low ratios of $|\dot{T}_c| / \dot{T}_{heating}$, resulting in a sharpening of the peak /self acceleration /. If the integral over the RTL intensity near T_g is independent on $|\dot{T}_c|$, then higher maximum intensity for lower $|\dot{T}_c|$ is obtained.

No attempts were made for a computer best fitting of the function $\Phi(\zeta)$ and the mixing parameter x. A first approximation for the spectrum $d\Phi(\zeta) / d \ln\zeta$ can be obtained directly from the glow curve, if we put $x=1$ and T is transformed into ζ according to eq.2 (DONTH , 1982). As indicated by preliminary mechanical experiments (DONTH et al. 1983) , the width of glow curve near T_g corresponds to the width of the dynamical glass transition zone (DONTH et.al 1979).

We can conclude that RTL glow curve near T_g in our statistical PBS copolymer can be well described in terms of glass transition phenomenology if we include the influence of cooling rate prior to excitation. The glow curve in this region is governed mainly by general properties of the relaxation process and the details of the kinetics of the electron transport and of the nonradiative recombination play only a minor role.

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