

Relaxation Properties of Styrene–Butadiene Block Copolymers. A Comparative Study of Thermally Stimulated Currents and Thermoluminescence

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Synopsis

The thermoluminescence (TL) and thermally stimulated current (TSC) curves observed in styrene–butadiene block copolymers, undoped and doped with different dyes, have been compared in order to test to what extent the thermoluminescence phenomenon can be correlated with intrinsic relaxation properties of the macromolecular chains. Generally, good agreement has been found between the two types of curves. However, the observance of a significant shifting of TL peaks as a function of the nature of the added dye shows that strict correspondence between the kinetics of the two phenomena is unlikely. Consequently, it seems actually dangerous to deduce the characteristic relaxation parameters of the polymer from TL curves.

INTRODUCTION

The thermally stimulated current (TSC) method, based on the discharge current curves obtained during heating of dielectrics previously polarized at a high temperature with a dc field, is now extensively used to study the molecular relaxation properties of polymers in the solid state.^{1–5} On the other hand, thermoluminescence (TL) of irradiated polymers is also generally considered as related to intrinsic relaxation processes, the macromolecular chains being considered effective carrier traps and the recombinations giving rise to TL peaks being essentially determined by chain motions. Consequently, it must be possible to establish more or less strict correlations between the results obtained by these two methods as well as between those obtained from more classical relaxation methods such as NMR and mechanical or dielectric loss measurements.

Such comparative studies are found for some polymers,^{6–9} and good agreement has generally been claimed between the positions of peaks obtained in TL and by dynamic methods. However, owing to the large differences in effective measurement frequencies used in the different methods, we already have pointed out that such correlations are only valid if extrapolations are made taking into account the shifting of the peaks as a function of frequency or heating rate.^{10,11} The corrections made, it is then often observed that good correlations are no more obvious to obtain. So, we have shown that in certain polymers such as polydi-*an*carbonate, the agreement between TL and other methods is poor and that the type of impurity contained in the matrix can play a prevailing role in the appearance of TL peaks.¹¹ Agreement in peak positions is better for other polymers such as ethylene–vinyl acetate copolymers,¹² but then the TL peak properties do not generally correspond to those of molecular relaxation processes.

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In this paper, we report the case of a styrene-butadiene block copolymer, undoped and doped with different dyes, for which the TL spectra obtained after UV or γ -irradiation show also good but not complete correlations with the relaxation properties as determined by the TSC method.

EXPERIMENTAL

The polymer studied is a commercial radial block copolymer of styrene-butadiene (Solprene 416, Phillips Petroleum) with a total styrene content of 30 wt-% and a density of 0.94 g/cc. This polymer contains trans, cis, and vinyl polybutadiene units (respectively 51, 36, and 13 wt-%, respectively, of the total butadiene content).

Doping was made by swelling the polymer in solvent-nonsolvent mixtures containing the dye. The dye content in the dried sample is always lower than 0.1%.

The experimental device used for recording the thermally stimulated currents is a classical one and has been described in a previous paper.¹³ The thermal cycles of polarization and depolarization applied to the samples consist essentially of the following steps: (1) heating to a temperature $T_p = 110^\circ\text{C}$, higher than the glass transition temperatures of the two homopolymers; (2) application of a dc electric field, $E_p = 14 \text{ kV/cm}$ for a time $t_p = 10 \text{ min}$; (3) rapid cooling in the field to a temperature $T_0 = -196^\circ\text{C}$; (4) cutting off the external field and linear heating ($b \simeq 5^\circ\text{C/min}$) of the samples shorted through an electrometer.

The polymer samples are used in the form of 1.4-mm-thick plates supplied with aluminum electrodes evaporated in vacuum.

For TL experiments, irradiations were always performed under vacuum at -196°C using either a 500-W xenon lamp (XBO) without monochromatization, either a 80-Ci ^{60}Co γ -source. The samples, 1.4 mm thick, are linearly heated at a rate of 10°C/min , adopted for technical reasons related to the temperature programmer used (Palcor RNS 9).

RESULTS AND DISCUSSION

Thermally Stimulated Currents

The TSC spectrum of undoped Solprene (Fig. 1) is composed of three distinct peaks characterized by very different intensities. At the heating rate used, their maximum temperatures T_M can be approximately situated at -150°C (β -peak), -87°C (α -peak), and $+65^\circ\text{C}$ (ρ -peak).

The β -peak, widely spread between -190° and -100°C , is probably composed of two or more overlapping, poorly resolved peaks. It corresponds well to the low-temperature complex peaks observed in pure polybutadiene by dynamic mechanical measurements of Morgan et al.¹⁴ and ascribed by these authors to local motions involving only the trans units of the polymer. Morgan et al. have pointed out the possibility of two distinct mechanisms to explain the structure observed, i.e., a crankshaft motion of the trans monomeric units and a complex twisting motion involving rotations about four backbone carbon atoms along with distortions of bond angles.

The α -peak has a maximum temperature close to the glass transition temperature of polybutadiene ($T_g \simeq -90^\circ\text{C}$) and can thus be attributed to confor-

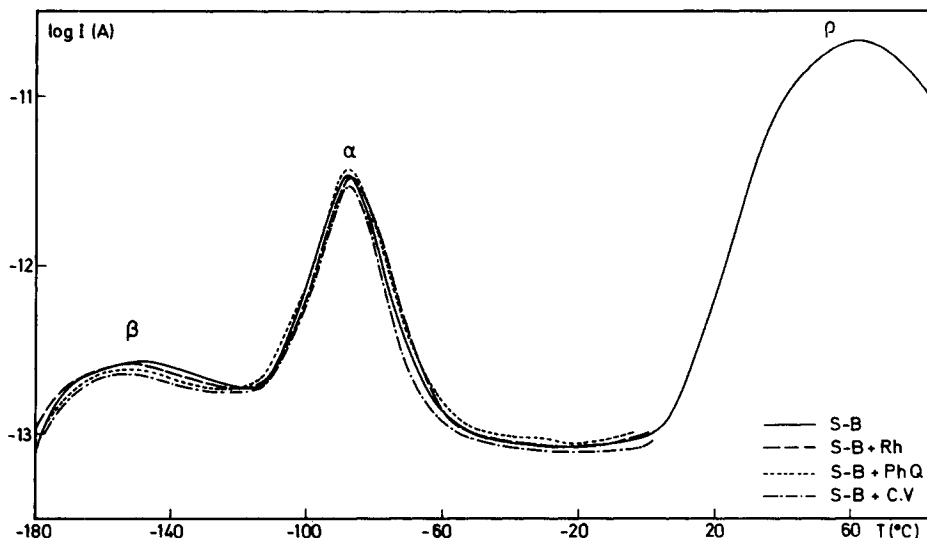


Fig. 1. TSC spectra of styrene-butadiene copolymer undoped (SB) and doped with rhodamine 6G (Rh), 9,10-phenanthrenequinone (PhQ), and crystal violet (CV): (—) SB; (---) SB-Rh; (.....) SB-PhQ; (- · - · -) SB-CV.

mation motions of main-chain segments occurring in the continuous elastomeric phase. It corresponds to the mechanical loss peak observed in the same temperature range in polybutadiene by low-frequency measurements.¹⁵

The ρ -peak does not seem related to any known intrinsic transition of polybutadiene or polystyrene entities. On account of its high intensity, it is probably of ionic origin. In fact, the maximum temperature of this peak corresponds well to the temperature where the mobility of the polystyrene regions increases substantially giving rise, for example, to an abrupt decrease in tensile strength¹⁶ or in the stress-optical coefficient.¹⁷ Consequently, it seems reasonable to attribute this TSC peak to the breakup of an ionic polarization resulting from a space charge accumulation at the polybutadiene-polystyrene interfaces.

The α - and β -regions of the TSC spectra of the copolymer doped with three different dyes (crystal violet, phenanthrenequinone, and rhodamine 6G) are shown in Figure 1. No significant difference appears with respect to the undoped sample.

Thermoluminescence

The thermoluminescence (TL) curves observed for undoped and dye-doped copolymers are shown in Figure 2 (TL after UV irradiation) and Figure 3 (TL after γ -irradiation). For undoped samples, they are in good agreement with TL results of Zlatkevich obtained in pure polybutadiene samples.¹⁸ In rhodamine- and crystal violet-doped samples, the TL intensity observed after UV or γ -irradiation is relatively little affected by the presence of dyes. In phenanthrenequinone-doped samples, on the other hand, the dopant has a marked influence either on the β -range of γ -irradiated samples (important decrease of the β -peak) or on the α -range of UV-irradiated samples (increase of the α -peak by more than one order of magnitude) (Table I).

Except for a slight shifting of peaks to high temperatures, the TL spectra fit rather well the TSC curves in the β - and α -range. Thermoluminescence in this

TABLE I
Maximum Intensities (I_M) and Maximum Temperatures (T_M) of Thermoluminescence Peaks Observed in UV- and γ -Irradiated Styrene-Butadiene Block Copolymer^a

Samples	UV-Irradiated				γ -Irradiated			
	β -Peak		α -Peak		β -Peak		α -Peak	
	I_M	T_M , °C	I_M	T_M , °C	I_M	T_M , °C	I_M	T_M , °C
SB	0.25	-135	0.44	-75	4.0	-120	3.0	-74
SB-CV	0.34	-135	0.54	-74	2.9	-120	6.1	-74
SB-Rh	0.26	-125	0.43	-69	4.1	-115	10.2	-70
SB-PhQ	0.65	-120	12.20	-64	1.3	-115	10.5	-66

^a The copolymers were undoped (SB) or doped with crystal violet (CV), phenanthrenequinone (PhQ), or rhodamine 6G (Rh). The I_M values are given in arbitrary units.

polymer can thus be probably ascribed, at least in part, to a detrapping process determined by the motions involved in the β - and α -transitions of the polybutadiene phase.

The activation energies, determined for undoped samples by the classical method of initial rise on a series of curves obtained during successive partial heatings,¹⁹ increase continuously from 4 to 6 kcal/mole in the β -range and from 6 to 24 kcal/mole in the α -range (Fig. 4). These values are compatible with molecular relaxation processes, and the evolutions observed must then be interpreted by the existence of important distributions of relaxation times, a fact often encountered in polymers on account of large differences in molecular environment of the motional units.

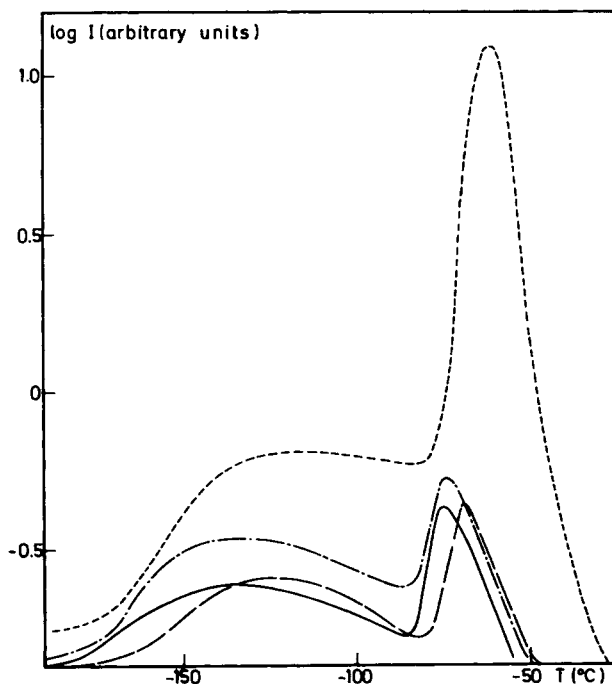


Fig. 2. TL spectra of styrene-butadiene copolymer obtained after 30 sec of UV irradiation: (—) SB; (---) SB-PhQ; (- - -) SB-Rh; (· · ·) SB-CV.

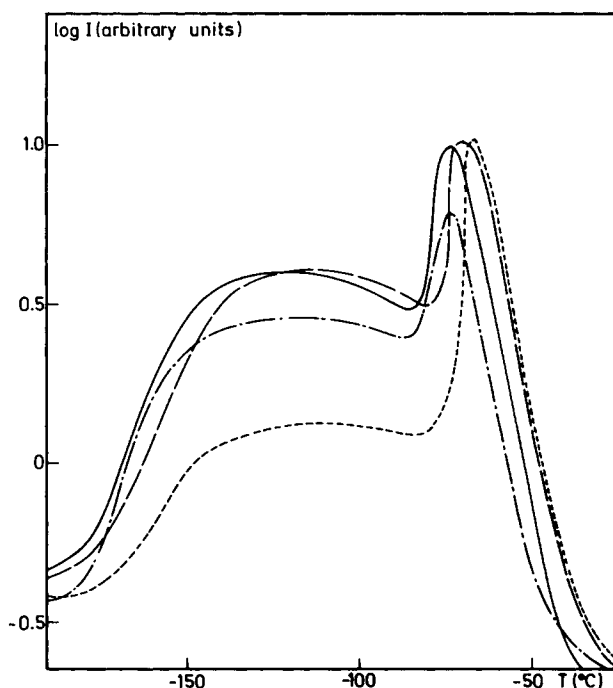


Fig. 3. TL spectra of styrene-butadiene copolymer obtained after 4×10^3 Rad γ -irradiation: (—) SB; (---) SB-PhQ; (---) SB-Rh; (- · -) SB-CV.

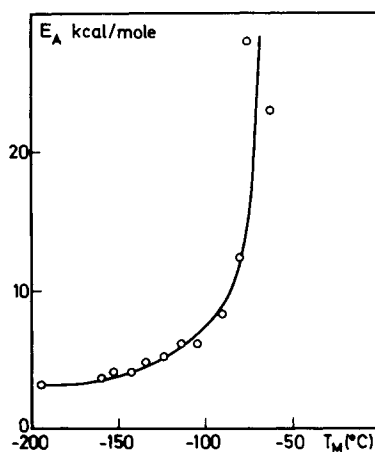


Fig. 4. Activation energies of the TL peaks as function of the maximum temperatures reached during the successive partial heatings.

Some remarks need, however, be made showing that the kinetics involved are not strictly identical in TL and TSC phenomena.

Because of the large activation energies involved, especially for the α -relaxation, the general shifting of the TL peaks to the high temperatures with respect to the TSC peaks cannot be explained only on the basis of differences in heating rates used ($5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$ in TSC and TL experiments, respectively). Contrary to the TSC results, the maximum temperatures of the TL peaks are significantly dependent on the nature of the added dye. On the other hand, the

maximum temperatures of the α -peaks are remarkably insensitive to the excitation mode (UV and γ -irradiations) and are thus characteristics of the dopant-polymer system (Table I). Lastly, it is obvious from Table I that the relative intensities of TL α - and β -peaks depend on the dopant used; then, the fact that whatever the dopant, no variation of resolution appears in the β -region seems to indicate that, contrary to the β -relaxation seen by dynamic methods, the TL β -peak is not complex in spite of its wide spread in a large temperature range.

These facts show that the carrier detrapping is not only governed by thermal motions of the polymer units but depends probably also of trapping parameters related to interactions between a particular dopant and the macromolecular chains.

CONCLUSIONS

A good agreement has been found between TL and TSC curves of styrene-butadiene block copolymers, showing that the recombination processes giving rise to thermoluminescence are at least partially determined by the carrier detrapping produced in the course of macromolecular chain motions. However, as shown by the shifting of the TL peaks and their dependence on the nature of added dyes, the kinetics involved in the two phenomena cannot be considered as strictly identical. Consequently, it is hardly to be expected that the characteristic parameters deduced from such TL curves can be unambiguously related to molecular motions; such parameters are rather hybrid values involving molecular relaxation parameters and trapping parameters particular to a given dopant-polymer system.

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References

1. J. van Turnhout, *Polym. J.*, **2**, 173 (1971).
2. D. Chatain, P. Gautier, and C. Lacabanne, *J. Polym. Sci., Phys.*, **11**, 1631 (1973).
3. P. Fischer and P. Röhl, *J. Polym. Sci., Phys.*, **14**, 531 (1976).
4. C. Ponevski and C. Solunov, *J. Polym. Sci., Phys.*, **13**, 1467 (1975).
5. S. I. Stupp and S. H. Carr, *J. Appl. Phys.*, **46**, 4120 (1975).
6. J. H. Ranicar and R. J. Fleming, *J. Polym. Sci., Phys.*, **10**, 1979 (1972).
7. A. E. Blake, A. Charlesby, and K. J. Randle, *J. Phys. D*, **7**, 759 (1974).
8. V. G. Nikol'skii and N. Ya Buben, *Dokl. Akad. Nauk SSSR*, **134**, 134 (1960).
9. M. Kryszewski, H. Kasica, J. Patora, and J. Piotrowski, *J. Polym. Sci. C*, **30**, 243 (1970).
10. A. Linkens and J. Vanderschueren, *J. Polym. Sci.*, **B15**, 41 (1977).
11. A. Linkens and J. Vanderschueren, in *New Prospects of the Theoretical Formulation of Thermally Stimulated Processes in Solids*, Intern. Workshop., Montpellier, 1976, to appear.
12. A. Linkens, J. Vanderschueren, S. Han Chor, and J. Gasiot, *Eur. Polym. J.*, **12**, 141 (1976).
13. J. Vanderschueren, in *Electrets, Charge Storage and Transport in Dielectrics*, M. M. Perlman, Ed., The Electrochem. Soc., Princeton, 1973, p. 155.
14. R. J. Morgan, L. E. Nielsen, and R. Buchdahl, *J. Appl. Phys.*, **42**, 4653 (1971).
15. G. V. Vinogradov, E. A. Dzyura, A. Ya. Malkin, and V. A. Grechanovskii, *J. Polym. Sci. A2*, **9**, 1153 (1971).
16. T. L. Smith and R. A. Dickie, *J. Polym. Sci.*, **C26**, 163 (1969).

17. E. Fischer and J. F. Henderson, *J. Polym. Sci.*, **C26**, 149 (1969).
18. L. Y. Slatkevich, *Rubb. Chem. Technol.*, **49**, 179 (1976).
19. H. Gobrecht and D. Hofman, *J. Phys. Chem. Solids*, **27**, 509 (1966).

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