Radiothermoluminescence as a Method for the Analysis of Structural Transitions in Polymers

INTRODUCTION

Detailed observations of the radiothermoluminescence of organic substances initiated by Nikolskii and Buben[1] and Charlesby and Partridge[2] in the early 1960s have been expanded in following years by many investigators.[3] One of the most significant results is the relative independence of the temperature of the glow peaks and overall shape of the glow curve on the nature and concentration of additives.[2–8] Since the luminescence is first order with respect to the trapped electron concentration, the intensity of the luminescence is determined by the rate at which the trapped electrons are being released. It can be concluded that the traps from which the electrons are being released before recombination are identical for polymers with and without additives. Therefore, these electron traps are not associated with additives but with the polymer chains themselves.[3] There has been considerable speculation about the nature of the trapping sites, but it is generally agreed that they are intermolecular in origin. The most generally accepted theoretical model is based on electron localization in cavities or voids that are associated with structural imperfections in the disordered solids.[9]

In many cases, the polymer itself does not give any significant luminescence. In those cases, the observed emission is from an impurity or from additive molecules attached to or contained in the polymer. However, the charge trapping is due mainly to the basic polymer structure. An erosion of the traps is induced by the onset of local motion in the polymer and involves only molecules located in the immediate vicinity of the electron trap. Thus, thermoluminescence is associated with the onset of various forms of molecular motion. Consequently, irradiated polymers will exhibit luminescence maxima during heating at temperatures corresponding to structural transitions occurring in the polymers.

The above brief description of the nature of radiothermoluminescence in organic substances is well established. The technique is supported by many researchers. This allows one to conclude that radiothermoluminescence is a useful method for locating and studying molecular motion and structural transitions in polymers. Indeed, it is routinely used for this purpose in some laboratories.[3]

Recently, however, Linkens and Vanderschueren questioned the use of radiothermoluminescence as a method for structural transition analysis.[10–12] Three objections were underlined by the authors:

(1) The difficulty of interpreting some of the radiothermoluminescence maxima on the basis of a relaxation mechanism.

(2) Nonisothermal measurements (the radiothermoluminescence and the other static methods) have very low equivalent frequencies in comparison to dynamic methods. A correlation between the two types of methods can be made only after extrapolation of dynamic measurements to low frequencies (10^{-2} to 10^{-4} Hz).

(3) The type of impurity contained in a polymer can play a prevailing role in thermoluminescence, and an observed glow curve is often typical of the dopant–polymer system.

Let us consider each of these objections separately.

(1) The appearance of a transition obtained by radiothermoluminescence and not by another testing method does not mean that this new transition is a result of processes other than those attributed to molecular relaxation. Furthermore, it was shown by Magat that all thermoluminescence peaks coincide with any and all reorganization of the organic matrix.[13] The discrepancy in the results obtained by different methods (or various modifications of the same method) is well known and depends on the relative sensitivity of the methods to the devitrification of a particular kind of mo-
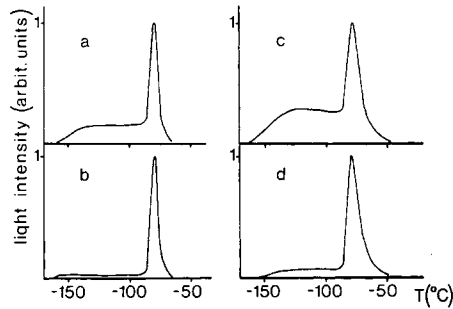
0021–8995/80/0025-0963$01.00

Fig. 1.   Glow curves for Solprene 233 (a), Solprene 233 doped with Ph (b), Solprene 416 (c), and Solprene 416 doped with Ph (d).

lecular motion.[14] For instance, comprehensive and combined analysis of dilatometric, calorimetric, dynamic mechanical, and electron spin resonance results led Boyer[15] to the conclusion that polyethylene exhibits three low-temperature structural transitions (LTST) around −120, −80, and −30°C. Only one or two LTST (from −196 to 0°C) are usually observed in polyethylene by dynamic spectroscopy.[16] On the other hand, three LTST whose positions coincide well with Boyer's estimate have been repeatedly shown to exist in polyethylene by the radiothermoluminescence technique.[2,17]

(2) Dynamic isothermal methods register a sample response at a certain chosen frequency. Thus, the temperature position of each transition can be attributed to this frequency. The comparison of the dynamic mechanical data covering a broad frequency range (10^{-3} to 30 Hz) and the radiothermoluminescence data for crude rubber[18] showed that the equivalent relaxation frequency in the glass transition region measured by radiothermoluminescence lies at 0.1–1.0 Hz. This frequency is significantly higher than that recommended by Linkens and Vanderschuern. However, a properly chosen equivalent frequency concept can be applied only to a particular structural transition. In static, nonisothermal experiments various molecular motion frequencies will usually correspond to structural transitions located at different temperatures. Therefore, it is inappropriate to try to make an overall correlation between dynamic data obtained at a certain frequency (whatever it is) to the radiothermoluminescence results where each subsequent transition might have a different effective frequency.

(3) A majority of the experiments described by Linkens and Vanderschuern[10-12] were done using ultraviolet light as the exitation source. Consequently, these experiments cannot be considered as a pure radiothermoluminescence test, since radiothermoluminescence requires high-energy ionizing irradiation. Furthermore, differences should be expected between the thermoluminescence curves after exposure to ionizing and ultraviolet irradiation, especially for polymer–dopant systems. The first interacts with the whole matrix in a statistically equivalent manner (no selectivity of absorption

TABLE I
Temperatures of Thermoluminescence Maximum for Undoped and Doped Polymers

Samples	Temp., °C	
	Roll milling[a]	Solvent immersion[a]
Solprene 233	−79	−79.5
Solprene 233 and CV	−79	−80
Solprene 233 and Rh	−79.5	−79
Solprene 233 and Ph	−78.5	−79
Solprene 416	−78	−78
Solprene 416 and CV	−77.5	−78
Solprene 416 and Rh	−78	−77.5
Solprene 416 and Ph	−77.5	−78

[a] Method of preparation.

peculiar to one particular type of molecule), whereas the latter is only absorbed by individual chromophores and aromatic impurities. The only experiment reported by Linkens and Vanderschuern with high-energy ionizing irradiation was performed with Solprene 416, a styrene–butadiene block copolymer doped with three different dyes: crystal violet (CV), phenanthrenequinone (Ph), and rhodamine 6G (Rh).[11] Since the basic conclusion concerning a prevailing role of the type of impurity contained in a polymer on its thermoluminescence was quite different from the results obtained by other investigators, we decided to reproduce Linkens and Vanderschuern's experiments.

EXPERIMENTAL AND RESULTS

In addition to Solprene 416, Solprene 233 (a polybutadiene homopolymer with the structure similar to the polybutadiene blocks in Solprene 416) was analyzed. Doping was performed by two methods: (1) the polymer was kept in the solution (methanol:toluene = 9:1) saturated with the dye for 28 hr and then dried in air; and (2) 0.1 wt % of the dye was roll milled directly into the polymer.

Irradiation was performed under vacuum at $-196°C$ to a dose of 1 Mrad using ^{60}Co as γ source. The installation used for thermoluminescence registration was similar to one described previously with a linear heating rate of $10°C/min$.[19]

Similar glow curves have been obtained for the samples doped by swelling and roll milling for all polymer–dopant systems studied. Practically no differences in the overall glow curve shape has been found between the glow curve for undoped samples and samples doped with Rh and CV. Similar to Linkens and Vanderschueren's observation, Ph-doped samples showed a noticeable relative decrease in glow intensity in the temperature region from -150 to $-90°C$ (Fig. 1). However, it is important to note that the doping with Ph was accompanied by a change in sample color during and just after preparation. For instance, Solprene 416 roll milled with Ph turned from yellow (the color of Ph) to pink. Since the polymers with physically dispersed CV and Rh showed glow curves similar to undoped samples, it is logical to attribute the differences in relative thermoluminescence intensity between undoped samples and samples doped with Ph to the occurrence of a chemical reaction between Ph and other additives contained in or attached to the polymers.

The most important result of the present study that is different from the results of Linkens and Vanderschueren is a complete independence of the position of main thermoluminescence maximum (T_g region) for either the polymer/dye combinations or the method of incorporation of the dye (Table I). For both polymers, with and without dyes, secondary relaxation (temperatures below $-90°C$) was spread over a wide temperature region. This made their temperature designation difficult. Accordingly, only T_g values are shown in Table I.

From the results of our experiments, it has been verified that additives dispersed into a polymer matrix do not have any significant influence on the positions of the thermoluminescence maxima and the overall glow curve shape. Consequently, radiothermoluminescence can be applied as a method for structural transitions analysis in polymers without interferences owing to possible sample contamination.

References

1. V. G. Nikolskii and N. Ya. Buben, *Proc. Acad. Sci. USSR Phys. Chem.,* **134,** 827 (1960).

2. A. Charlesby and R. H. Partridge, *Proc. R. Soc. London Ser. A,* **271,** 170 (1963).

3. R. H. Partridge, in *The Radiation Chemistry of Macromolecules,* Vol. 1, M. Dole, Ed., Academic, New York, 1972, Chap. 10.

4. J. M. Rozman, *Bull. Acad. Sci. USSR Phys. Ser.,* **22,** 50 (1958).

5. L. F. Pender and R. J. Fleming, *J. Phys. C,* **10,** 1571 (1977).

6. R. J. Fleming and L. F. Pender, *J. Electrostat.* **3,** 139 (1977).

7. N. Ya. Buben, V. I. Goldanskii, L. Yu. Zlatkevich, V. G. Nikolskii, and V. G. Raevskii, *Vysokomol. Soedin. Ser. A,* **9,** 2275 (1967).

8. I. Boustead and A. Charlesby, *Proc. R. Soc. London Ser. A,* **315,** 271 (1970).

9. J. Jortner, *Radiat. Res. Suppl.* **4,** 24 (1964).

10. A. Linkens and J. Vanderschueren, *J. Electrostat.* **3,** 149 (1977).

11. A. Linkens and J. Vanderschueren, *J. Appl. Polym. Sci.,* **22,** 3081 (1978).

12. A. Linkens and J. Vanderschueren, *J. Polym. Sci. Part B,* **15,** 41 (1977).

13. M. Magat, *J. Chem. Phys.,* **63,** 142 (1966).

14. R. F. Boyer, *Polymer,* **17,** 996 (1976).

15. R. F. Boyer, *Macromolecules,* **6,** 288 (1973).

16. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* Wiley, London, 1967, p. 355.

17. V. G. Nikolskii, L. Yu. Zlatkevich, M. B. Konstantinopolskaya, L. A. Osintseva, and V. A. Sokolskii, *J. Polym. Sci., Polym. Phys. Ed.,* **12,** 1267 (1974).

18. V. G. Nikolskii, *Sov. Sci. Res.,* **3,** 77 (1972).

19. L. Yu. Zlatkevich and V. G. Nikolskii, *Rubber Chem. Technol.,* **46,** 1210 (1973).

Northern Petrochemical Company
Technical Center
Morris, Illinois 60450

L. Y. ZLATKEVICH
L. F. NICHOLS
N. T. CRABB