

## THE THERMAL LIGHT EMISSION PROPERTIES OF ALATHON 1 EFFECT OF EXPERIMENTAL PARAMETERS\*

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### ABSTRACT

DSC and light emission (LE) curves were obtained in nitrogen, air, and oxygen atmospheres between 300 and 700 K for Alathon 1, a cube-cut polyethylene molding powder. In air and oxygen, light-emitting as well as thermal degradation reactions showed the expected dependence on oxygen concentration. In nitrogen, initial light emission was shown to involve oxygen absorbed in the polymer sample. Upon depletion of the latter, less intense light emission was observed indicating a different light emitting reaction. Between 385 and 460 K an activation energy of  $80 \text{ KJ mol}^{-1}$  was estimated for light-emitting reactions in  $\text{N}_2$ ,  $\text{O}_2$  and air atmospheres. Evidence of a first-order dependence on oxygen concentration was also obtained.

### INTRODUCTION

The light emission (LE) of polymers when they are heated has been observed by numerous investigators<sup>1-4</sup>. The earliest definitive report of this phenomenon<sup>1</sup> involved a study of polypropylene between 40 and 180°C. It was noted that the light intensity was proportional to oxygen concentration, decreased by the presence of antioxidants, and not detectable in the absence of oxygen. Similar light emission has been observed<sup>2</sup> for polypropylene and polycarbonate in oxygen between 100 and 300°C. Moreover, polypropylene, in the presence of dicumyl peroxide, was shown to emit light at 150°C, even in a nitrogen atmosphere<sup>3</sup>. As a result, it has been widely felt that the emission of light in such thermally stimulated reactions is somehow connected to the formation of peroxy radical intermediates. The latter, of course, depends upon oxygen concentration. An element of contradiction was introduced by the results of a study of the simultaneous DTA and light emission of various polymers by David<sup>4</sup>. He noted that a weak light emission was observed from 200 to 400°C for polyethylene, polystyrene, poly(methyl methacrylate), and polyvinyl chloride. The possibility of oxygen leakage into the system was suggested.

In consequence of the foregoing, several questions arise. First, does light

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emission actually occur when a polymeric material is heated above room temperature in nitrogen? Second, if so, is the transformation from which light emission results the same in both nitrogen and oxygen? Third, what relationship exists between the light emission and enthalpic changes? This investigation addresses itself to these questions. After studying numerous polymers, the optimum combination of light intensity and temperature range over which the light emission occurred was obtained from Alathon 1, a cube-cut polyethylene molding powder. This polymer was selected to study the effects of the experimental parameters of gaseous atmosphere, heating rate, sample size, and so on, on the light emission curves.

## EXPERIMENTAL PART

### *Material*

Alathon 1, a cube-cut polyethylene molding powder, a product of the E. I. DuPont de Nemours Co., Wilmington, Dela.

### *Apparatus*

Light emission (LE) curves were obtained using an SSR Model 1105 Photon Counter equipped with a Model 1120 Amplifier Discriminator and a Model 1150 PMT Housing. The latter contained a 1P28 photomultiplier tube operated at 750 volts. The background dark count was about 60 counts per second. The PMT was mounted directly on the glass plate top of the sample holder assembly cover of the Perkin Elmer DSC-1B. Such an arrangement was quite satisfactory at sample temperatures of less than 560 K. As the sample temperature was increased above this temperature, however, thermionic emission became increasingly significant. It was found that the range of measurement could be extended by as much as 100 degrees by removing the PMT from the sample holder assembly cover and using a light pipe. Unfortunately, this arrangement suffered from two disadvantages. First, the amount of light reaching the PMT was appreciably less than in the other arrangement so that weak light-emitting transitions frequently escaped detection. Second, the polymer occasionally contracted in size or otherwise changed position in the sample pan when undergoing a reaction which resulted in mis-alignment of the sample with the end of the light pipe so that the PMT response dropped to that of the background. The PMT response in counts per second has been given the symbol  $R$ . In some cases the background response ( $R_b$ ) was subtracted to give the quantity,  $R - R_b$ . A third quantity, noted as  $R_t$ , is the product of  $(R - R_b)$  in counts per second and  $t$ , the time in seconds.

DSC curves were obtained simultaneously with the light emission curves using the Perkin-Elmer DSC-1B calorimeter. Although of great value in correlating major enthalpic changes with light emitting reactions, these curves suffered from drastic and uncontrollable baseline deviations. As a consequence, the curves obtained on a DuPont Model 990 DSC using different samples are presented here. Unless otherwise noted, all observations were made at a heating rate of  $20^\circ\text{C min}^{-1}$ . All purge gases were dried by passage through a concentrated  $\text{H}_2\text{SO}_4$  bubbler tube.

## RESULTS AND DISCUSSION

The DSC and LE curves for Alathon 1 in nitrogen, air, and oxygen atmospheres are shown in Fig. 1.

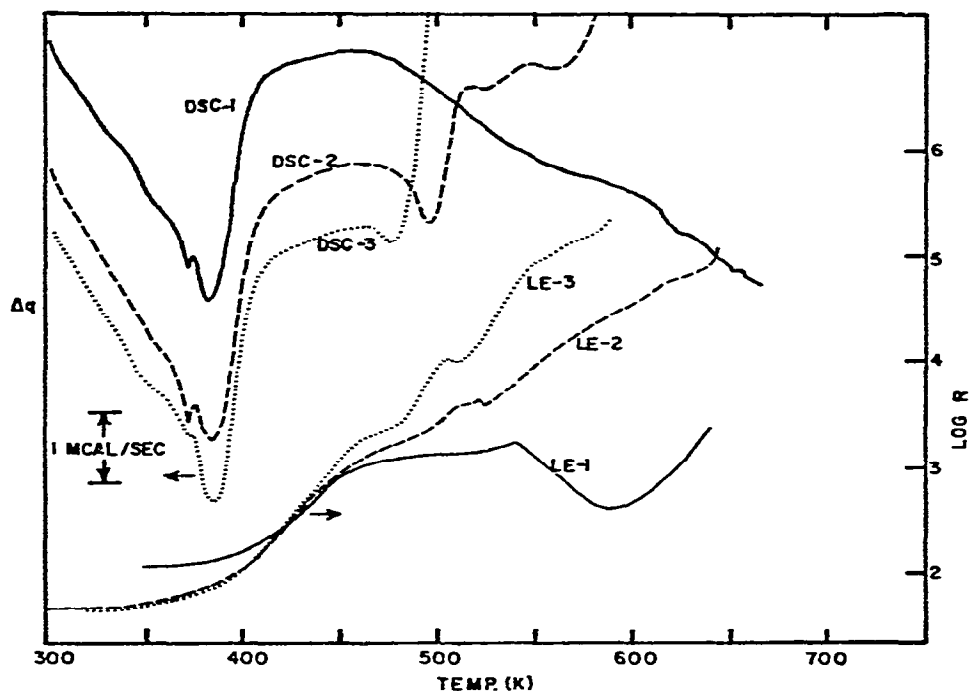


Fig. 1. DSC and LE curves of Alathon 1. DSC-1, 22.8 mg in  $N_2$ ; DSC-2, 25.7 mg in air; DSC-3, 21.9 mg in  $O_2$ ; LE-1, 24.5 mg in  $N_2$ ; LE-2, 23.7 mg in air; LE-3, 24.8 mg in  $O_2$ .

The DSC curves are virtually identical in all three of the atmospheres in the temperature range of 300 to 475 K, during which the sample melted. The LE curves in the same temperature range are not substantially affected by the nature of the atmosphere. At 475 K in oxygen and 495 K in air, a strongly exothermic degradation reaction began which was accompanied by light emission. These curves suggest that at least two steps are involved. In nitrogen, a slow endothermic change above 475 K was accompanied by some light emission, the intensity of which was much less than that in air and in oxygen and which decreased markedly above 540 K.

It is generally accepted that the thermal degradation of polymeric materials involves a free radical process<sup>5</sup> initiated by the generation of polymer-free radicals ( $P\cdot$ ). In the presence of  $O_2$ , the formation of hydroperoxide radicals ( $PO_2\cdot$ ) or molecules ( $PO_2H$ ) are possible resulting in the following termination steps:

- (1)  $2P\cdot \rightarrow$  products
- (2)  $PO_2\cdot + P \rightarrow$  products
- (3)  $2PO_2\cdot \rightarrow$  products +  $O_2$

At high  $O_2$  concentrations, step (3), thought to involve ketonic intermediates, is the most significant while at low  $O_2$  concentrations, step (1) predominates. Light emission, or chemiluminescence, accompanies all three termination steps. Light emission associated with steps (2) and (3), known as oxyluminescence, is considerably more intense than that arising from step (1)<sup>6</sup>.

For Alathon 1, the light emission as well as the nature of chemical transformations above 475 K depend on the concentration of oxygen present. The similarity among LE curves between 300 and 475 K suggests the occurrence of the same phenomenon in all three gases. On the basis of several observations, reports of which follow, it is felt that oxygen, which is initially present in the nitrogen atmosphere, produces an oxyluminescent type of reaction until effectively consumed at about 475–500 K. Subsequent, light emission in nitrogen must result from a  $[2P \cdot \rightarrow \text{products}]$  type chain termination and will be designated herein simply as chemiluminescence. This inference is supported by the results presented in Fig. 2. For

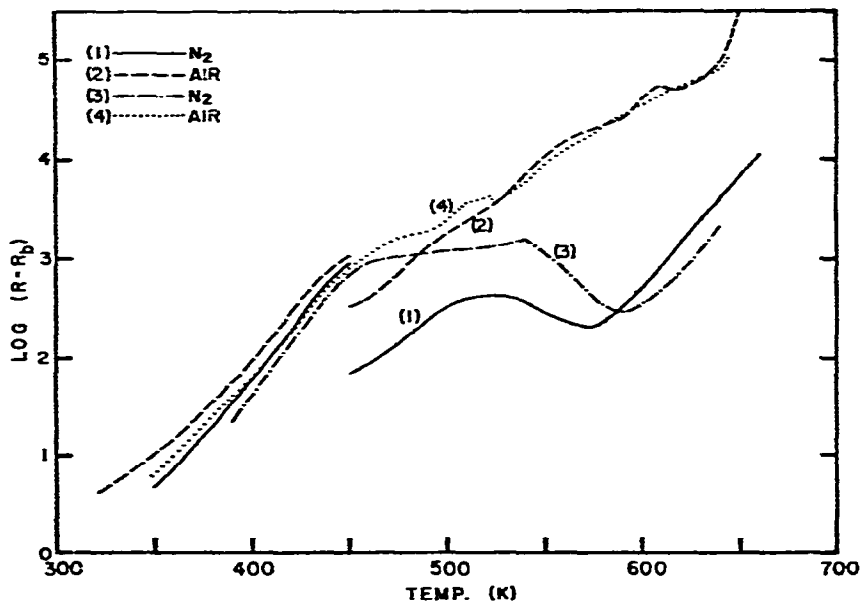


Fig. 2. LE curves of Alathon 1. Curve 1, 28.3 mg,  $N_2$ ; curve 2, 23.3 mg, air; curve 3, 24.5 mg,  $N_2$ ; and curve 4, 23.7 mg, air.

samples represented by curves (1) and (3), the heating program was interrupted at 450 K for 32 min, while curves (2) and (4) were taken from Fig. 1. During the isothermal period, light emission decreased in intensity in both purge gases, the decrease in air being substantially less than that in nitrogen. Upon reinstatement of the heating program, high intensity light emission (oxyluminescence) gain occurred in air but not in nitrogen.

The rate at which light emission occurs,  $-dn/dt$ , is directly dependent on some function of the number of reactive sites ( $n$ ) and the concentration of  $O_2$ , if the latter

is involved, or:

$$-\frac{dn}{dt} = Kn^a(O_2)^b$$

where  $K$  is a constant,  $n$  is the number of reactive sites, and  $a$  and  $b$  are orders with respect to  $n$  and  $O_2$ , respectively. In addition, the direct relationship between light emission intensity and reaction rate is generally given as:

$$(R - R_b) = \alpha\phi \left( -\frac{dn}{dt} \right)$$

where  $(R - R_b)$  is the PMT response minus the background response,  $\alpha$  is a constant, and  $\phi$  is the quantum efficiency. In this study, a constant value of  $\phi$  over temperature ranges of interest was assumed. The time dependence of the reaction rate for Alathon I at 450 K (the isothermal period in Fig. 2) is shown in Fig. 3. The initial and relatively rapid decrease in rate probably corresponds to the completion of the first major

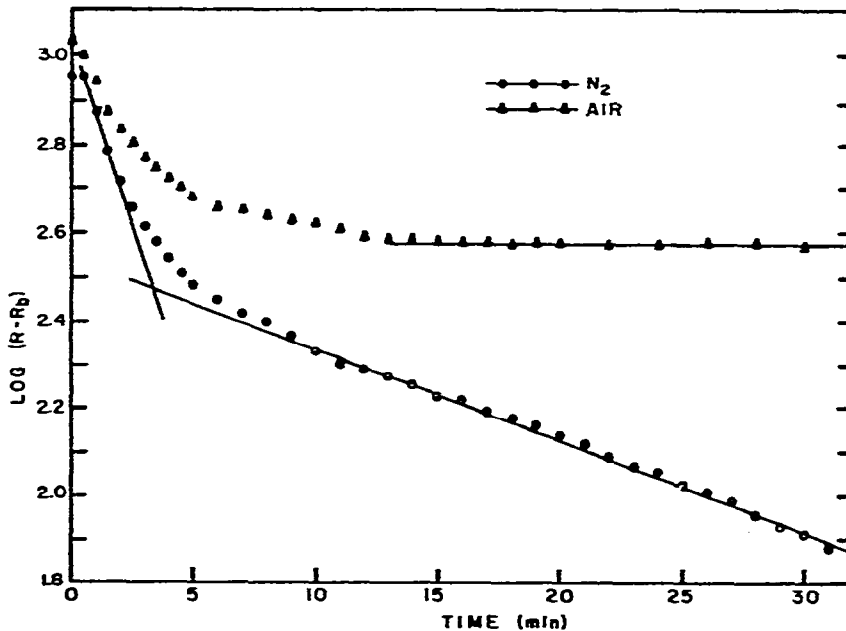


Fig. 3. Change in  $(R - R_b)$  with time for Alathon I at 450 K.

light-emitting step (475 K in Fig. 1). The rate of the subsequent light-emitting step becomes essentially constant in air but undergoes a slow decrease in nitrogen. In a dynamic air atmosphere, the concentration of oxygen is constant and variations in reaction rate can result only from a change in the number of reactive sites, i.e.:

$$-\frac{dn}{dt} = K'n^a$$

This leads to the conclusion that the light-emitting reaction which occurs in air is sufficiently slow and that the value of  $n$  is virtually constant. Since the value of  $n$  would be expected to decrease no faster in  $N_2$  than in air, the decrease in reaction rate in  $N_2$  must represent the depletion of  $O_2$ , or:

$$-\frac{dn}{dt} = K^n(O_2)^b$$

Furthermore, the linear relationship between the logarithm of the rate and time indicates a first-order dependence such that:

$$-\frac{dn}{dt} = K^n(O_2)$$

Acceptance of near constancy of  $n$ , at least over short temperature and time intervals, provides an additional benefit. It becomes possible to attribute most of the change in reaction rate (light intensity) during the heating program to a temperature dependence. As a result, plots of  $(R - R_0)$  versus  $1/T$  should permit the estimation of the activation energy,  $E$ , wherein no assumption of reaction order with respect to  $n$  is necessary. This, of course, is the basis for the well-known "initial rise" method. Such a plot is presented for Alathon 1 in Fig. 4. Between 385 and 460 K it is apparent that

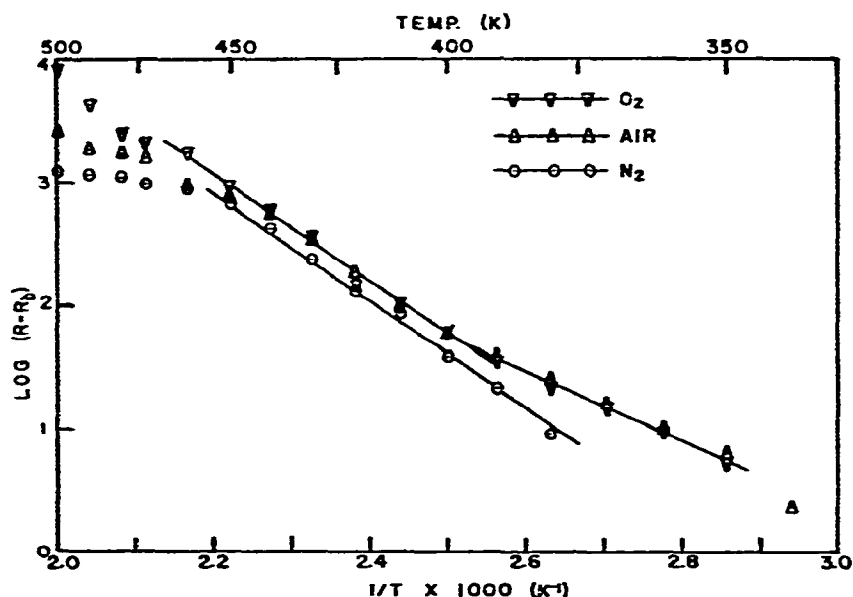


Fig. 4. Change of  $(R - R_0)$  with temperature for Alathon 1 in various atmospheres.

the same reaction occurs in all three atmospheres and that its activation energy is about  $80 \text{ KJ mol}^{-1}$ . Of interest also is the indication that two separate reactions occur between 300 and 460 K, although an unusually intense background response precludes the observation of the reaction in nitrogen between 300 and 385 K.

The source of oxygen when nitrogen is used as the purge gas is a question of considerable interest. Leakage into the system makes no more than a very minor contribution. In several instances, the PMT response in nitrogen decreased to that of the background after an initial emission of light. This behavior was especially pronounced in the case of some nylon samples which were also studied. Entrapment of air when the system was closed was not a source of a significant amount of oxygen. Light-emission curves obtained after flushing the system with nitrogen for as much as 90 min prior to a heating did not differ from those obtained without prior flushing. Hence, oxyluminescence in the early stages of light emission in nitrogen must result from oxygen absorbed by the polymer. Experimental observations support this conclusion, several of which are summarized in Fig. 5. In this series of experiments, a single 23.4 mg sample of Alathon 1 was heated in nitrogen four times, being cooled to 300 K between each run. The initial LE curve [Curve (1)] is identical to its counterpart in Fig. 1. Upon reheating the sample without opening the system, very weak light emission, probably manifesting chemiluminescence, was obtained. Exposure of the cooled sample to air in the dark for 1/2 and 14 h [Curves (3) and (4), respectively] resulted in the increased light emission of oxyluminescence.

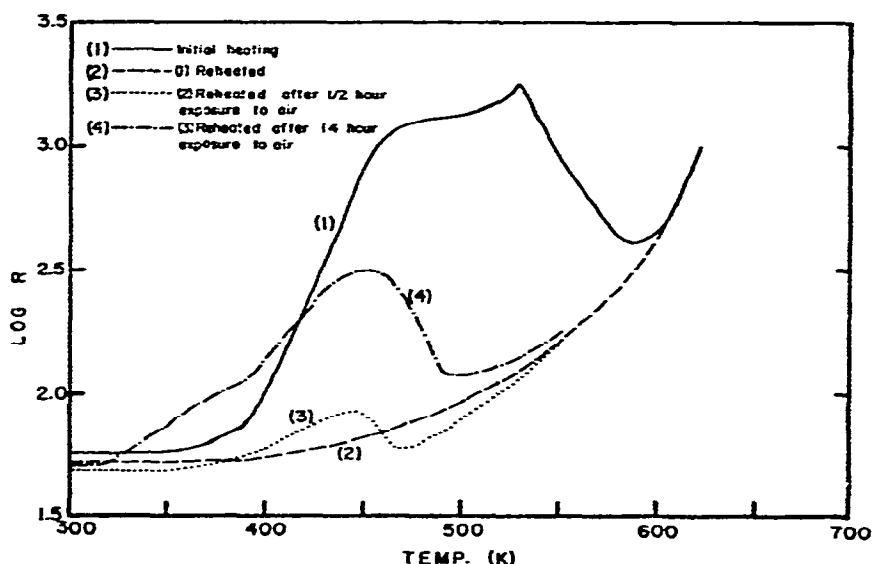


Fig. 5. LE curves of Alathon 1 under various conditions. Curve 1, initial heating; curve 2, same sample cooled to 300 K and reheated; curve 3, same sample reheated after standing in air for 0.5 h; curve 4, same sample reheated after standing in air for 14 h.

The relationship between the light emission and sample size for Alathon 1 are given in Fig. 6. The sample surface exposed directly to the PMT was about 10 mm<sup>2</sup> in each case although the total surface was 60, 40 and 30 mm<sup>2</sup> for the 24.5, 12.5, and 5.0 mg samples, respectively. The background response prevents a precise measurement of total light emission ( $R_t$ ) above 560 K but it appears that the latter approaches

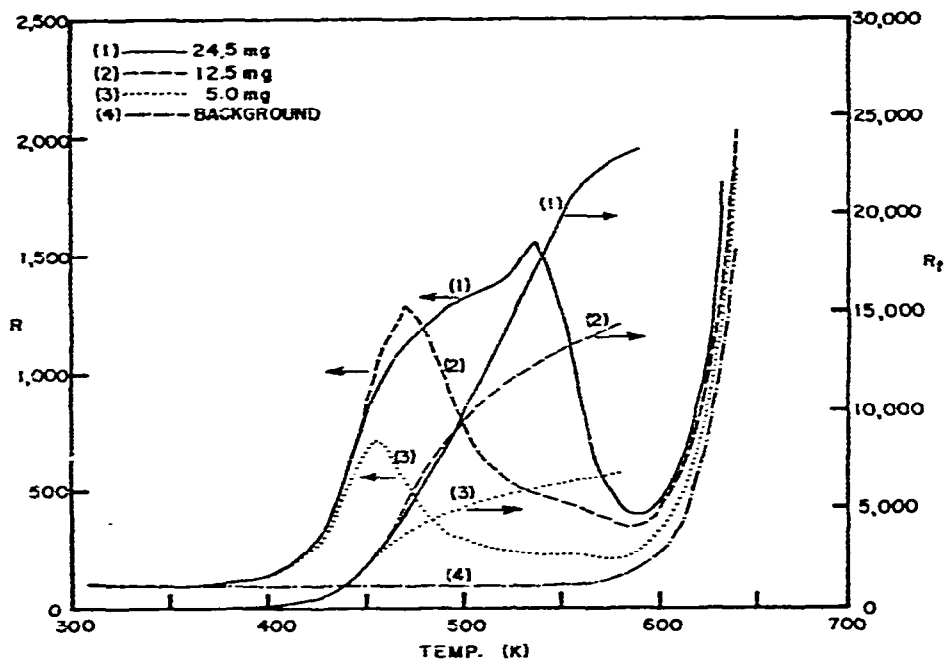


Fig. 6. Effect of sample size and surface area on the light emission of Alathon 1. Curve 1, 24.5 mg; 60 mm<sup>2</sup>; curve 2, 12.5 mg, 40 mm<sup>2</sup>; curve 3, 5.0 mg, 30 mm<sup>2</sup>; curve 4, background count.

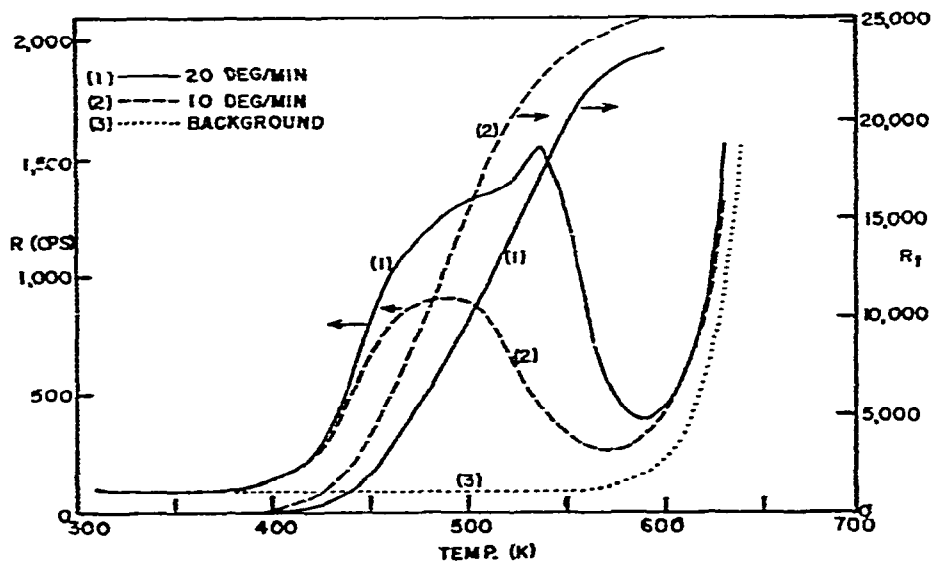


Fig. 7. Effect of heating rate on the light emission of Alathon 1. Curve 1, 24.5 mg, 20°C min<sup>-1</sup>; curve 2, 24.9 mg, 10°C min<sup>-1</sup>; curve 3, background.



a limit consistent with sample size and is not related to the sample surface. The amount of absorbed oxygen would also be a function of sample size. Since light emission starting at about 370 K is initially of much the same intensity for all samples, this means that in a large excess of absorbed oxygen the reaction rate is only temperature-dependent. Subsequent depletion of oxygen first retards the increase in reaction rate and then causes the latter to decrease.

The effect of a heating rate on the light-emission curves of Alathon 1 is shown in Fig. 7. At  $10^{\circ}\text{C min}^{-1}$ , the shape of the LE curve is quite unlike that obtained at  $20^{\circ}\text{C min}^{-1}$ , yet the total light emission is only slightly greater at the lower heating rate. It is felt that this manifests the same amount of absorbed oxygen in both samples with more extensive chemiluminescence after oxygen depletion at the slower heating rate (or longer heating time).

On the basis of these results, it is felt that light emission by Alathon 1, when heated in air or oxygen, is related to the presence of peroxy intermediates. Light emission in nitrogen, on the other hand, is much less intense and probably arises from simple free-radical combination. It must be recognized that regardless of the atmosphere, initial light emission involves oxygen to the extent that the latter is absorbed by the polymer sample.

Although melting is unaffected by the nature of the purge gas, initial light-emission reactions occurring in the same temperature range are dependent. The relationship between these early light-emitting reactions and the final chemical degradation, if any, is still unclear and merits additional study. In that the principal objective of this investigation was to study the effect of experimental parameters on the light-emission curves, the effect of such things as initiators, inhibitors, and catalysts has not been considered. Several of these may also result in the light emission of the Alathon 1 when it is heated in this temperature range.

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#### REFERENCES

- 1 G. E. Ashby, *J. Polym. Sci.*, 50 (1961) 99.
- 2 R. E. Barker, Jr., J. H. Daane and P. M. Rentzepis, *J. Polym. Sci.*, Part A, 3 (1965) 2033.
- 3 R. J. DeKock and P. A. H. M. Hol, *Rec. Trav. Chim.*, 85 (1966) 102.
- 4 D. J. David, *Thermochim. Acta*, 3 (1972) 277.
- 5 L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw Hill, New York, 1971, p. 99.
- 6 L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw Hill, New York, 1971 p. 161.