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THE THERMAL LIGHT EMISSION PROPERTIES OF VARIOUS POLYMERS

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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 samples of poly(ethylene), 66 Nylon, polycarbonate, poly(vinyl pyrrolidone), and poly(acrylonitrile). In all atmospheres, initial LE was the "oxyluminescence" type associated with the hydroperoxide radical formation; in nitrogen, after the depletion of absorbed oxygen, a much weaker "chemiluminescence" was observed.

INTRODUCTION

The emission of light by polymers when they are heated above room temperature has been the subject of numerous investigations[1-5]. Generally, such light emission has been associated with peroxy radical intermediates, the formation of which required the presence of oxygen[1-3]. In one case, light emission in nitrogen atmosphere was also reported[4].

In a recent paper[5], the present investigators reported the results of a DSC and light emission (LE) study of Alathon 1, a cube-cut poly(ethylene) molding powder. Evidence was presented for two separate light generating processes: in oxygen, a relatively intense "oxyluminescence" was observed; in nitrogen, a much less intense "chemiluminescence" occurred. The former was believed to manifest thermal degradation involving polymer peroxy radicals ($PO_2\cdot$) whereas the latter was attributed to a simple polymer free radical ($P\cdot$) mechanism[6]. It was shown that even in a nitrogen atmosphere, initial light emission was of an oxyluminescent type due to oxygen absorbed by the polymer sample.

In this report, the light emitting properties of eight additional polymeric materials are presented.

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EXPERIMENTAL PART

Materials

The eight polymer samples studied included:

(a) Ivithene, molded poly(ethylene) strip; (b) Nalgene, molded poly(ethylene) commercially available in the form of storage bottles; (c) 66 Nylon molding powder; (d) molded 66 Nylon strip; (e) molded 66 Nylon tubing; (f) molded polycarbonate tubing; (g) poly(vinyl pyrrolidone) molding powder; and (h) poly(acrylonitrile) molding powder.

LE apparatus

The LE apparatus was described previously[5]. All data were obtained at a heating rate of 20 deg min^{-1}. The photo-multiplier tube response in counts per second has been given the symbol R. In some cases, the background response (R_b) was subtracted and the quantity $R-R_b$, assumed to be the PMT response due only to sample, is reported.

RESULTS AND DISCUSSION

The DSC curves for Ivithene (Fig. 1) and Nalgene (Fig. 2) are similar to those reported[5] for Alathon 1. In oxygen and air, highly exothermic degradation reactions occurred above 455–475 K and were accompanied by intense light emission. Associated LE curves suggest two steps in this degradation. In nitrogen, the involvement of at least two light emitting steps is clearly indicated. The curves for Ivithene, shown in Fig. 3, indicate that the initial light emitting reaction (up to about 460 K) is the same in all three atmospheres. Its activation energy is about 41 kJ mol^{-1}. In air and oxygen, the highly exothermic degradation reaction which begins at about 460 K has an activation energy of approximately 199 kJ mol^{-1}. The non-linearity of $\log(R-R_b)$ vs. $1/T$ in nitrogen at temperatures greater than 460 K is taken as evidence of oxygen depletion in the latter. As a result, it is felt that light emission in nitrogen above 500–525 K from Ivithene and 450–475 K from Nalgene must largely manifest chemiluminescence.

The LE and DSC curves for 66 Nylon (Figs. 4–6) provide an additional insight into the effect of oxygen uptake. In the cases of the 66 Nylon molding powder (Fig. 4) and molded 66 Nylon strip (Fig. 5), the initial light emitting reactions were essentially complete at about 420 and 385 K, respectively. In nitrogen, the very weak light emission obtained thereafter is attributed to chemiluminescence. In air and oxygen atmospheres, rather intense light emission occurred above these temperatures. Of great interest is the appearance of a peak in the LE curves at the melting point, which is especially strong in the molded sample. It appears that following the initial reaction, light emission is a function not only of temperature but also of the rate at which oxygen is absorbed by the sample. Predictably, the latter is greater in pure oxygen and is enhanced by melting.

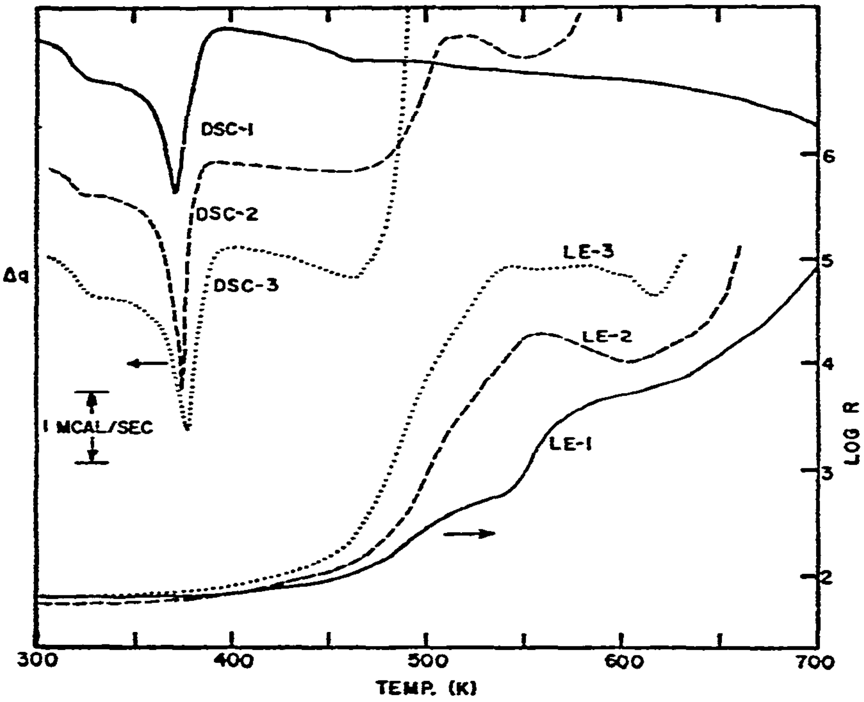

Fig. 1. DSC and LE curves of Ivithene. DSC-1, 7.4 mg in N_2; DSC-2, 7.6 mg in air; DSC-3, 7.5 mg in O_2; LE-1, 7.5 mg in N_2; LE-2, 7.4 mg in air; LE-3, 7.4 mg in O_2.

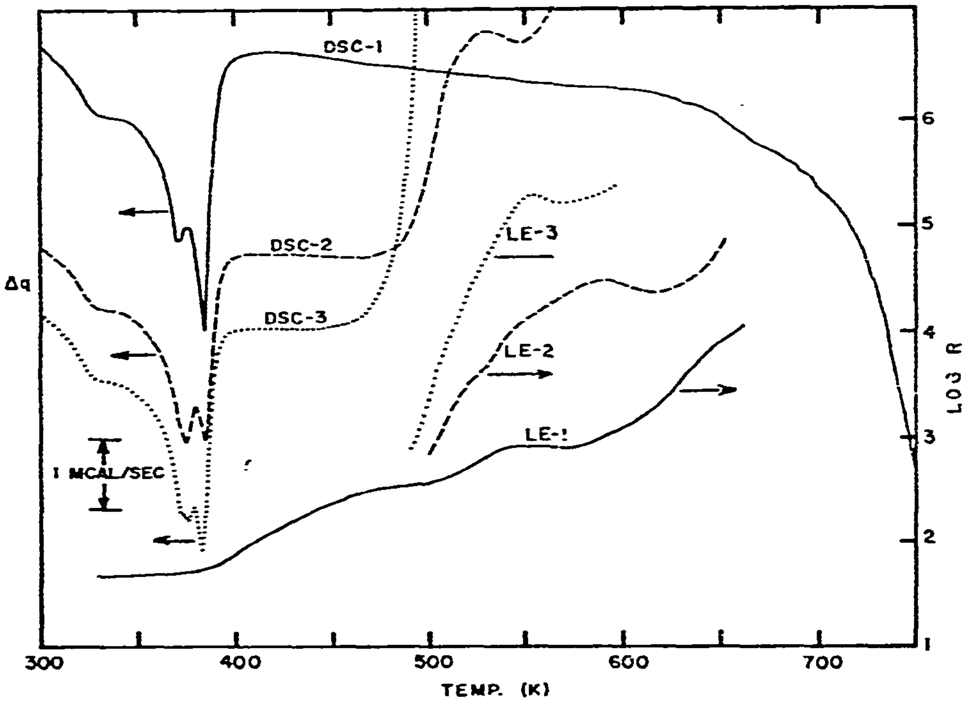

Fig. 2. DSC and LE curves of Nalgene. DSC-1, 12.4 mg in N_2; DSC-2, 11.4 mg in air; DSC-3, 10.9 mg in O_2; LE-1, 11.4 mg in N_2; LE-2, 12.1 mg in air; LE-3, 12.5 mg in O_2.

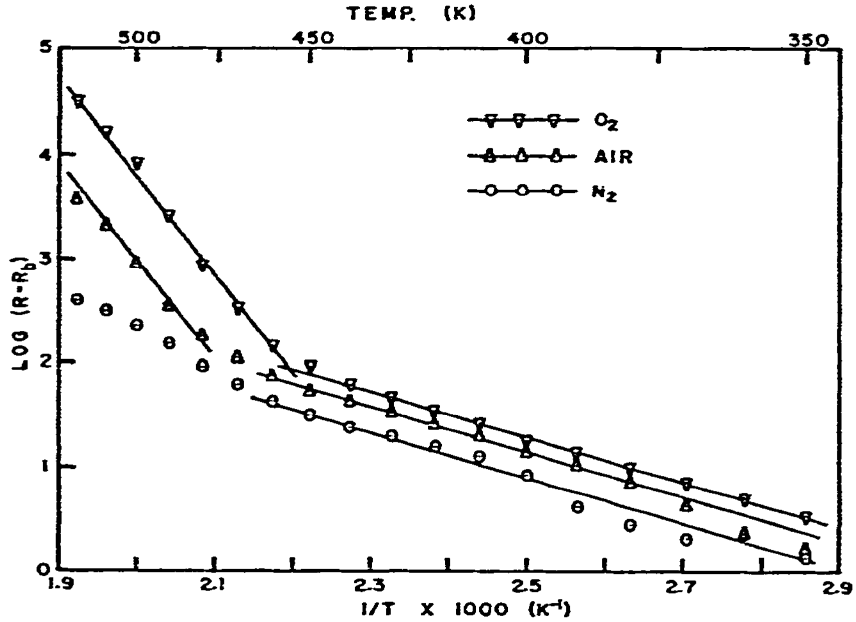

Fig. 3. Change of (R–R_0) with temperature for Ivithene in various atmospheres.

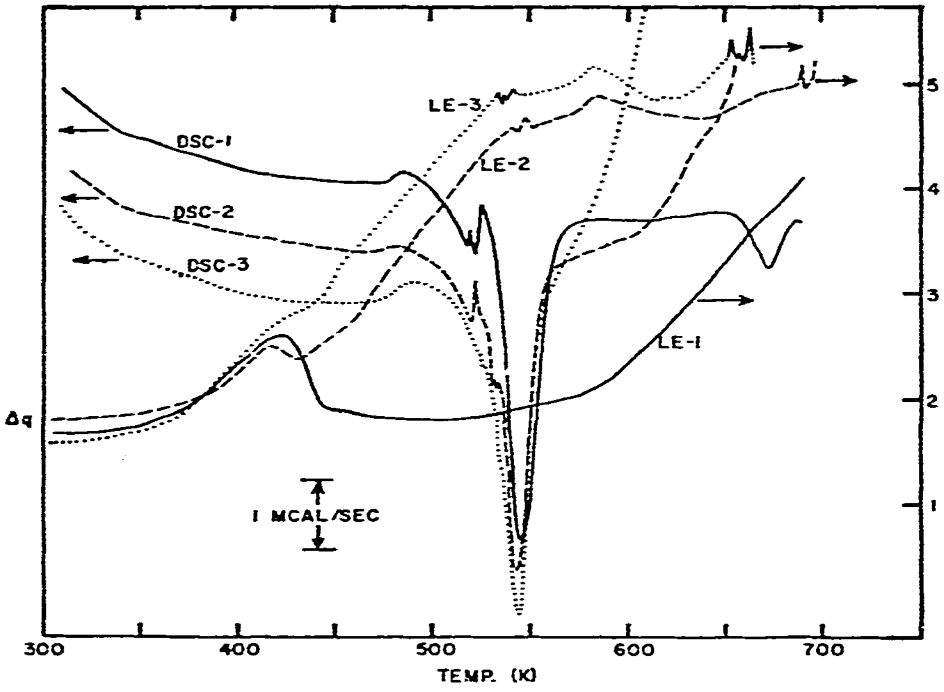

Fig. 4. DSC and LE curves of 66 Nylon molding powder. DSC-1, 25.4 mg in N_2; DSC-2, 21.0 mg in air; DSC-3, 20.9 mg in O_2; LE-1, 18.8 mg in N_2; LE-2, 9.7 mg in air; LE-3, 12.5 mg in O_2.

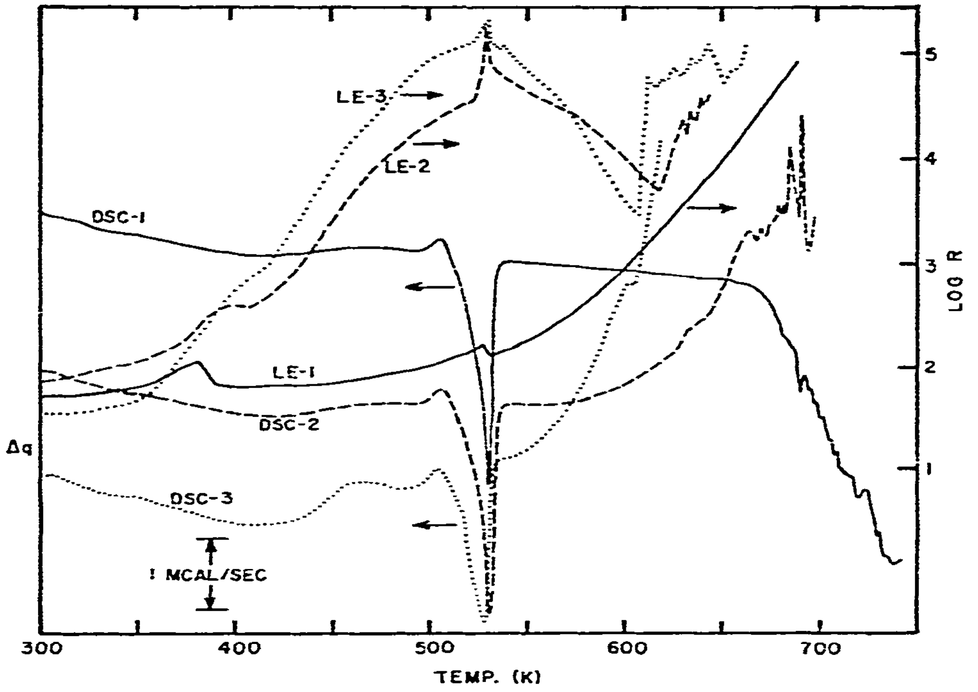

Fig. 5. DSC and LE curves of molded 66 Nylon strip. DSC-1, 6.1 mg in N_2; DSC-2, 6.3 mg in air; DSC-3, 6.4 mg in O_2; LE-1, 5.9 mg in N_2; LE-2, 6.3 mg in air; LE-3, 6.5 mg in O_2.

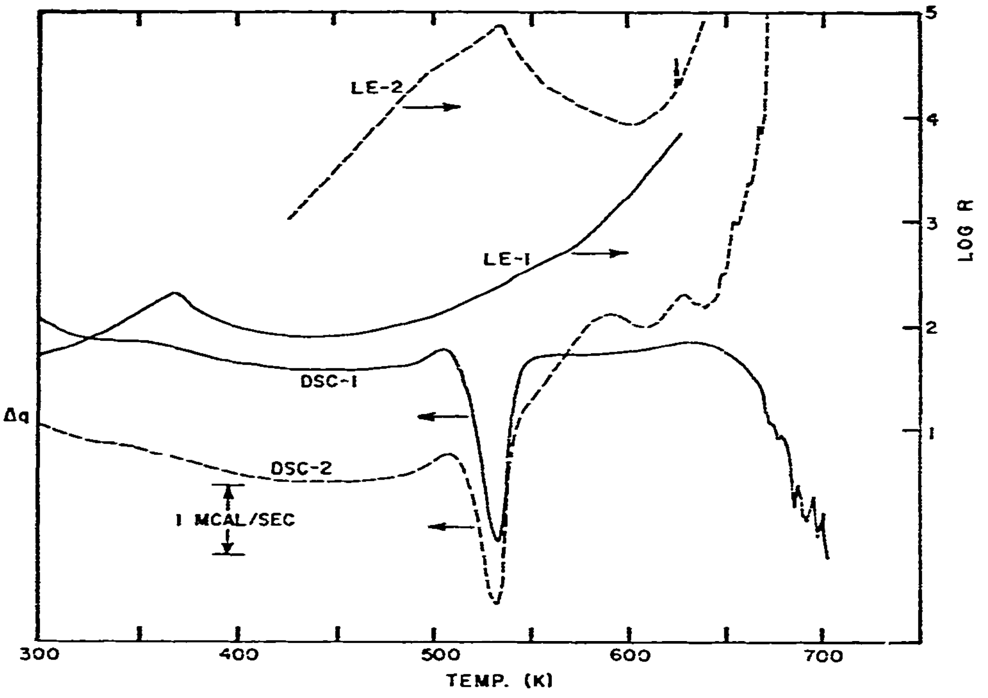

Fig. 6. DSC and LE curves of molded 66 Nylon tubing. DSC-1, 12.6 mg in N_2; DSC-2, 10.7 mg in air; LE-1, 12.7 mg in N_2; LE-2, 11.1 mg in air.

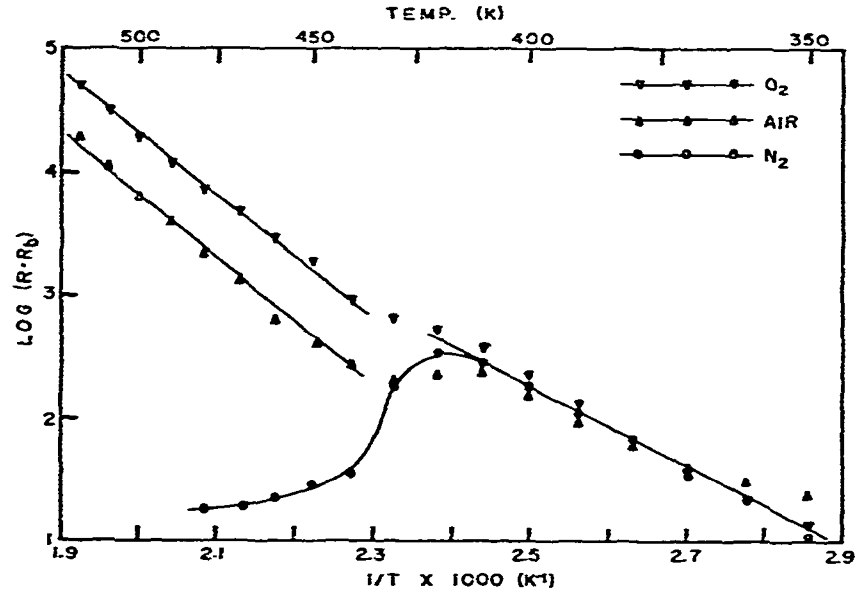

Fig. 7. Change of (R–R_b) with temperature for 66 Nylon molding powder in various atmospheres.

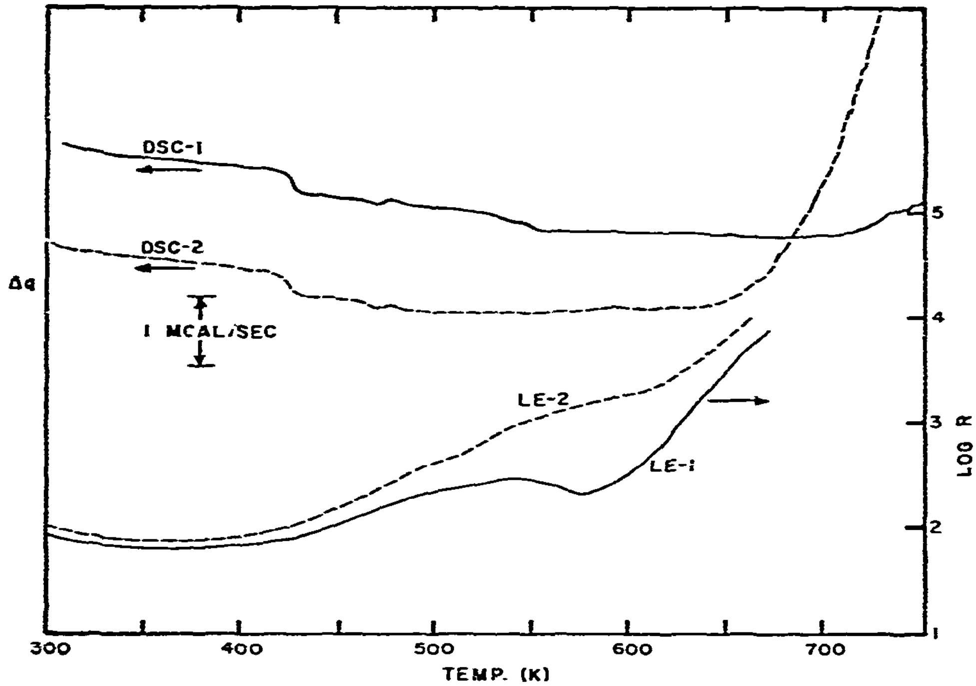

Fig. 8. DSC and LE curves of polycarbonate. DSC-1, 18.6 mg in N_2; DSC-2, 17.5 mg in air; LE-1, 21.0 mg in N_2; LE-2, 15.1 mg in air.

The results shown in Fig. 7 for the 66 Nylon molding powder indicate the same reaction in all purge gases up to a temperature of 420 K. The activation energy estimated for this reaction is 63 kJ mol^{-1}. Above 435 K, the reaction rate in nitrogen approaches zero. Although the reaction in air is slower than in oxygen, an activation energy of 97 kJ mol^{-1} is indicated in both atmospheres.

Except for a glass transition at 430 K, polycarbonate (Fig. 8) exhibited no enthalpic changes below 660 K. At that temperature, oxidative degradation occurred in air. The light emission curve of polycarbonate, which produced the weakest light emission observed in this investigation, again indicates the same reaction in nitrogen and air up to 480 K, where oxygen depletion in the nitrogen purge gas became significant.

The only truly powdered samples for which results are included here are poly(vinyl pyrrolidone) and poly(acrylonitrile). The DSC and LE curves for the former, given in Fig. 9, support observations already presented and can be interpreted much as those for other samples. Of particular interest here are the results shown in Fig. 10 for poly(vinyl pyrrolidone) heated in nitrogen. Curve (1) was obtained from a sample heated without prior treatment while curve (2) was obtained using a sample which had been kept under partial vacuum for 4 h prior to analysis. The effect of removing absorbed oxygen is clear. Curves (3) and (4) were obtained using disks of 11.8 and 2 mg, respectively, pressed at about 2700 atm. Maximum light emission by the latter occurred at lower temperatures than in the unpressed sample. Although peak light emission by both disks was much the same, it can be seen from curves (3) and (4) that total light emission by the heavier disk was considerably greater. Since they were of virtually the same surface area, it is evident that, as with Alathon 1 (ref. 5), total emission is much more a function of the amount of oxygen absorbed (reflected by sample size) than of the surface exposed.

The DSC curves for poly(acrylonitrile) (Fig. 11) are quite different from those already discussed. Endothermic transitions were not observed either in nitrogen or air atmospheres. In fact, this sample of poly(acrylonitrile) was characterized by a narrow exothermic transition at 540 K in nitrogen and a narrow, much more intense exothermic transition at 580 K in air. The fact that these transitions occurred at different temperatures and were of vastly different energies shows a clear dependence on the atmosphere. The LE emission curves for both samples are much the same until at 400 K the oxygen became depletted by the nitrogen purge gas. As noted in other polymer samples, subsequent light emission was considerably stronger in air. This sample provides almost unequivocal evidence that the difference in intensity results from different phenomena, i.e., oxyluminescence vs. chemiluminescence. Without question the two degradation reactions produce different products and the more exothermic reaction in air suggests more extensive oxidation. Such behavior would be completely consistent with the increased production of hydroperoxide free radicals or molecules prior to decomposition.

It is inferred that the results summarized here support our earlier conclusions[5]—namely, initial light emission in all atmospheres is the result of oxyluminescence

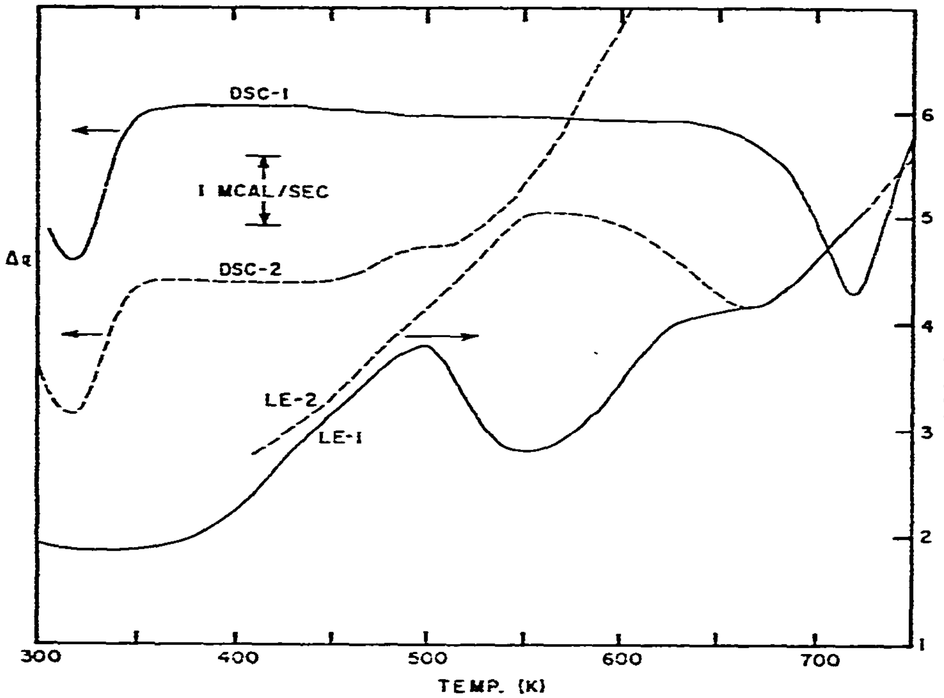

Fig. 9. DSC and LE curves of poly(vinyl pyrrolidone). DSC-1, 3.0 mg in N_2; DSC-2, 3.0 mg in air; LE-1, 3.0 mg in N_2; LE-2, 2.9 mg in air.

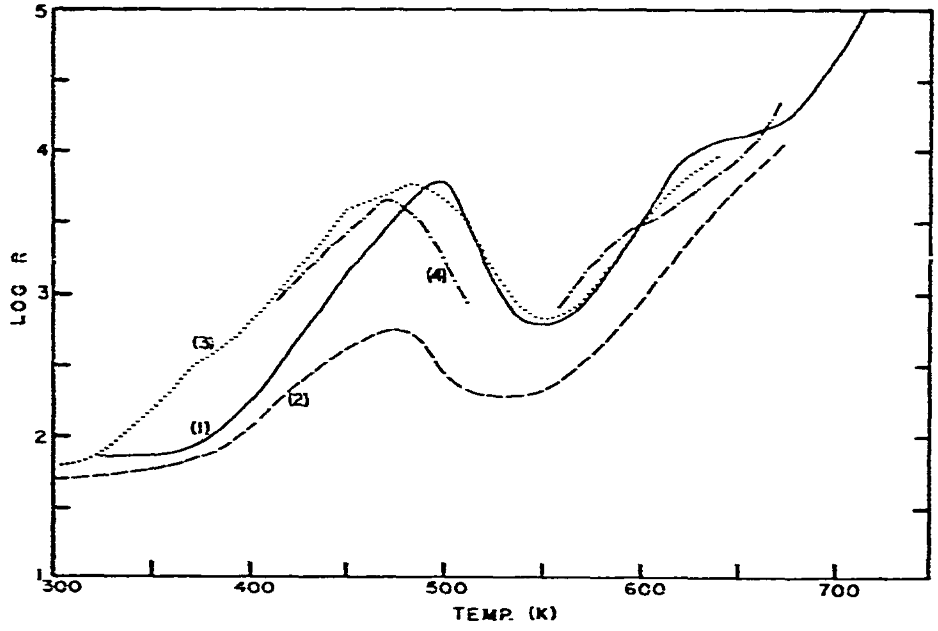

Fig. 10. LE curves of poly(vinyl pyrrolidone) in N_2. Curve 1, 3.0 mg powder; Curve 2, 3.3 mg powder; Curve 3, 11.8 mg disk; Curve 4, 2 mg disk.

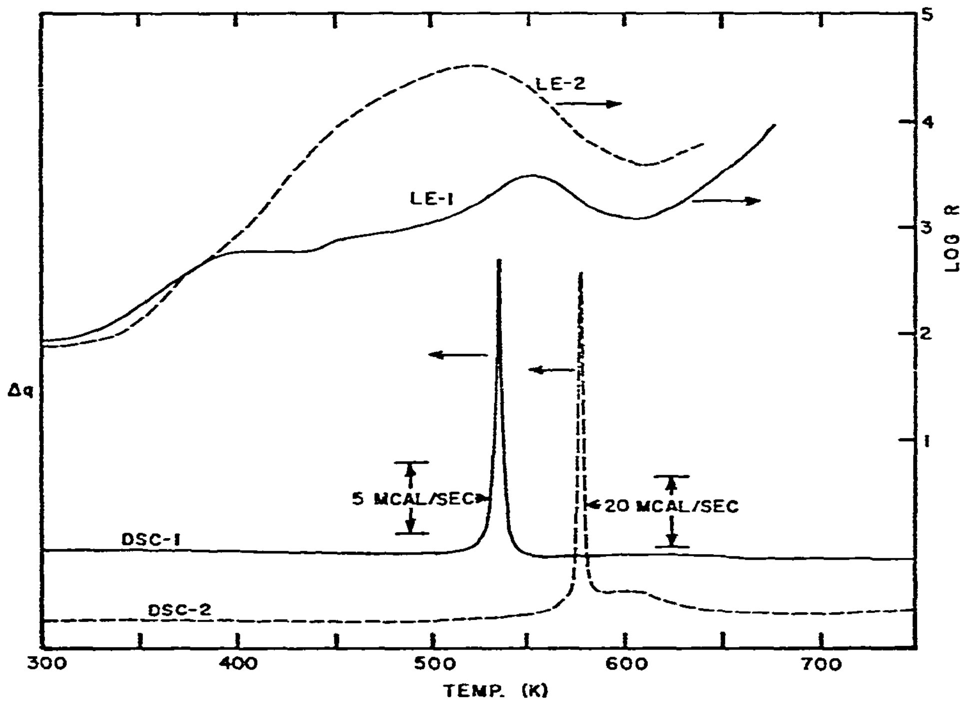

Fig. 11. DSC and LE curves of poly(acrylonitrile). DSC-1, 3.9 mg in N_2 : DSC-2, 4.0 mg in air: LE-1, 4.7 mg in N_2 : LE-2, 4.2 mg in air.

associated with the formation of hydroperoxide radical intermediates. Subsequent light emission in air and oxygen also manifests oxyluminescence: in nitrogen, however, it is the much weaker phenomenon, noted as chemiluminescence. Except for 66 Nylon, no correlation between light emission and melting point was observed. On the other hand, a clear relationship between light emission and the final chemical degradation exists and merits additional study. The effect of initiators, inhibitors, and catalysts in the polymeric materials also deserves further consideration.

ACKNOWLEDGMENTS

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REFERENCES

1 G. W. 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. K. DeKock and P. A. H. M. Hol. *Rec. Trav. Chim.*, 85 (1966) 102.
4 D. F. David, *Thermochim. Acta*, 3 (1972) 277.
5 A. M. Wynne and W. W. Wendlandt, *Thermochim. Acta*, 14 (1976) in press.
6 L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971, p. 161.