

Oxyluminescence of Polymers.

I. General Behavior of Polymers*

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Synopsis

The faint emission of light by various classes and types of polymers when heated in the presence of oxygen, oxyluminescence, was studied by means of a photomultiplier tube and sensitive microammeter. Among the polymers with a carbon-carbon backbone, the polymers having the greater number of tertiary carbon atoms generally showed greater intensities of luminosity. Polystyrene was a notable exception to this generalization. The shape of the luminosity versus time curves varied with the type of polymer. It was also found that the emission of light did not stop instantly when the oxygen atmosphere was replaced by an inert gas, but rather followed an exponential type of decay. The rate of decay appeared to be different with different types of polymers. The intensities of luminescence and the times required to reach maximum or steady state luminescence were compared with oxygen uptake data for various polymers. In general there was a qualitative, but not necessarily quantitative correlation between the luminous intensities and polymer stabilities in the presence of oxygen.

INTRODUCTION

The oxidative degradation of polymers is believed to proceed by a complicated series of consecutive radical reactions which are not entirely known or understood.¹ Any new phenomena which may aid in the study of this process are therefore of considerable interest and warrant investigation. Recently Ashby² reported the faint emission of light by various polymers on heating in air or oxygen. He termed this phenomenon "oxyluminescence."

It has long been known that many organic substances will emit light when slowly oxidized in solution under suitable conditions.³ Luminescent effects arising from the interaction of two radicals have also been known for many years.⁴ Recently Vasil'ev and his co-workers have studied the faint light emission by radicals produced by the thermal decomposition of azoisobutyronitrile,⁵ benzoyl peroxide, and other peroxides or hydroperoxides in hydrocarbon solutions.⁶ They found that those systems which were most strongly luminescent were those in which oxygenated radicals such as $\text{ROO}\cdot$ were present. They attributed the emission of light to an exothermic reaction in which the resulting "nonequilibrium excited states"

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became deactivated by emission of a quantum of light.⁷ They showed that on substitution of nitrogen for an oxygen atmosphere there was a decay of luminosity which they attributed to the reaction



It appears, therefore, that oxyluminescence should provide us with a fundamental tool for the study of polymer degradation once the phenomenon is understood. Ashby² has studied a variety of polymers and found that the emission of light varied considerably from type to type. Working principally with polypropylene, he found that the oxyluminescence varied with both antioxidant concentration and type. This suggested the use of oxyluminescence as a means of evaluating polymer stability. In order to determine what correlations exist between stability and oxyluminescence, it was decided to compare the oxyluminescence of various polymers with a conventional method of measuring stability, such as oxygen uptake⁸ studies. At the same time, this phenomenon was investigated in a general manner as a means of studying the oxidative degradation of polymers.

EXPERIMENTAL

Apparatus

The apparatus used for the study is shown in Figure 1. A 3-in. diameter sample (E) was placed on the surface of a thermostatically controlled heating block (G) inside a light-tight box. A ring with an optical glass cover provided a chamber (D) in which the sample could be heated under an inert gas, air, oxygen, or other desired atmosphere. The entering gas was metered by a rotameter and was heated by coils around the block (G). The flow rate for the admission of gas to the chamber was regulated by needle valves, and the use of a flow rate of 200 ml./min. permitted a rapid replacement of the gas atmosphere in the 60-ml. chamber over the sample.

The light emitted by the polymer passed up through glass filters (C), if any were used, the shutter opening (B), through a separated pair of windows which serve as a thermal barrier, and finally to the 1P21 photomultiplier tube (A) cathode. The current generated was measured by means of a micromicroammeter and recorded on one channel of a dual-channel recorder. The anode voltage was obtained from a bank of 90 v. batteries by using a combination of taps and a potentiometer for exact adjustment. With 1000 v. on the anode, the phototube had a luminous sensitivity of approximately 80 amp. per lumen in the region of maximum spectral response of $4000 \pm 500 \text{ \AA}$. For convenience, the data reported in this paper will give the luminosity in terms of the anode current generated as the same tube was used throughout these studies.

The phototube assembly was placed in a chamber filled with solid CO_2 and thermally insulated from the rest of the equipment. This permitted a

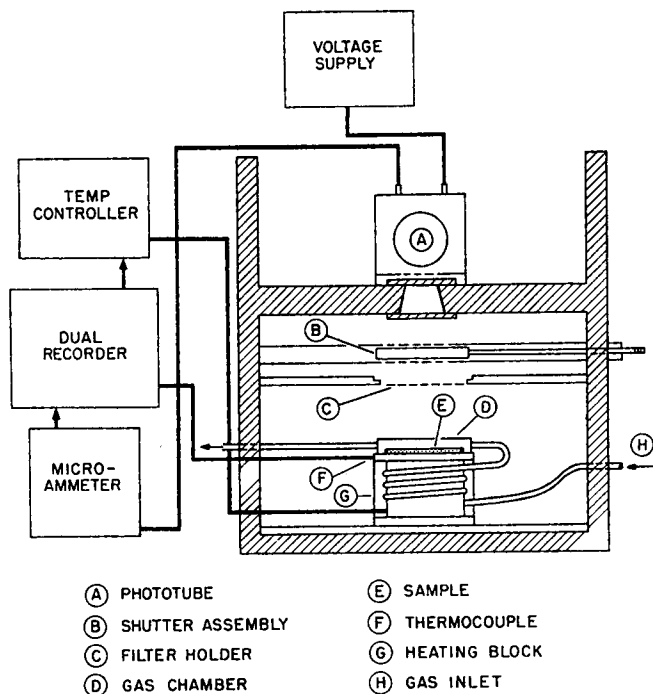


Fig. 1. Apparatus used.

reduction of the noise level and dark current to less than 1×10^{-11} amp. (about 10^{-13} lumens).

The second channel of the recorder was used to record the temperature. At the same time it sent an error signal to the temperature controller which controlled the temperature of the heating block to within $\pm 0.5^\circ\text{C}$.

Procedure

The polymer to be tested was compression molded into a sheet (usually 15 mils) from which the 3-in. circular samples were cut. The sample was then placed on the heating block with a nitrogen flow of about 200 ml./min. When the polymer was at the desired temperature (in most cases 150°C .), the nitrogen was turned off and oxygen or other gas was added as desired. This point was taken as t_0 for the luminosity versus time curves. The dark current could be checked at any time by closing the shutter.

The polymers used were commercial materials which were free of anti-oxidants and other additives except where noted.

The oxygen absorption studies were carried out in the conventional manner⁸ with the use of 10 mil sheets. The numerical data are given in terms of t_{10} , the time required for a gram of polymer to absorb 10 ml. of oxygen, since this has been found in the case of the polyolefins to result in severe degradation of the electrical and other properties.⁹

RESULTS AND DISCUSSION

In Table I are listed the maximum (or steady-state) luminosities, the times required to reach maximum luminosity, as well as the t_{10} 's obtained by oxygen absorption for various polymers. Generally the more stable polymers, as evidenced by the longer t_{10} 's, show a lower maximum or steady state luminosity. There are several exceptions to this generalization, particularly among polymers of different classes which have the same order of light emission intensities. From Table I it also appears that there is no correlation between the time to the maximum or steady-state luminosity, and the stability in oxygen. Among the polymers having a strictly carbon-carbon backbone structure, it appears that as the number of tertiary hydrogen atoms increases, so does the luminosity. It may be that oxyluminescence will prove to be a method for determining chain branching. An exception to this observation is polystyrene. Here it would appear that resonance and stabilization due to the aromatic ring play a significant role. Rather than emit the extra energy as light, it may act to absorb and redistribute energy in a manner similar to the way the aromatic ring tends to stabilize polystyrene to high energy radiation.¹⁰

TABLE I
Oxyluminescence of Polymers ($T = 150^\circ\text{C}$., Anode Voltage = 1000 v.)

Polymer	Maximum luminosity, amp.	Time to maximum luminosity, min.	t_{10} at 150°C ., hr.
Polytetrafluoroethylene	1.55×10^{-11}	~ 0	$>2000^a$
Polystyrene	6.90×10^{-11}	3	530 ^a
Polyethylene terephthalate	7.2×10^{-11}	~ 0	<2000
Polyethylene (H.D.)	1.2×10^{-10}	>180	—
Polyoxymethylene	1.5×10^{-10}	~ 0	(depoly.) ^a
Polyurethane	2.9×10^{-10}	<1	65
Polyethylene (L.D.)	6.7×10^{-10}	>120	1.8
Polymethyl methacrylate	9.5×10^{-10}	52	$>2000^a$
Nylon 66	3.0×10^{-9}	25	3
Nylon 6	7.8×10^{-9}	98	4
Nylon 610	1×10^{-8}	15	2
Polypropylene A	1.9×10^{-8}	37	0.8
Polypropylene C	2.2×10^{-8}	45	0.3
Polypropylene B	2.7×10^{-8}	50	0.3

^a Data obtained at 140°C . by P. G. Kelleher of these Laboratories.

The shapes of the luminous intensity versus time curves vary considerably from one polymer to another. The polymers which show a low intensity of oxyluminescence, such as polyoxymethylene, polystyrene, and polyethylene terephthalate, show a very rapid build-up of luminosity when oxygen is admitted, reaching a maximum within a minute or so, then falling off and gradually approaching steady-state conditions (Fig. 2). Polymers

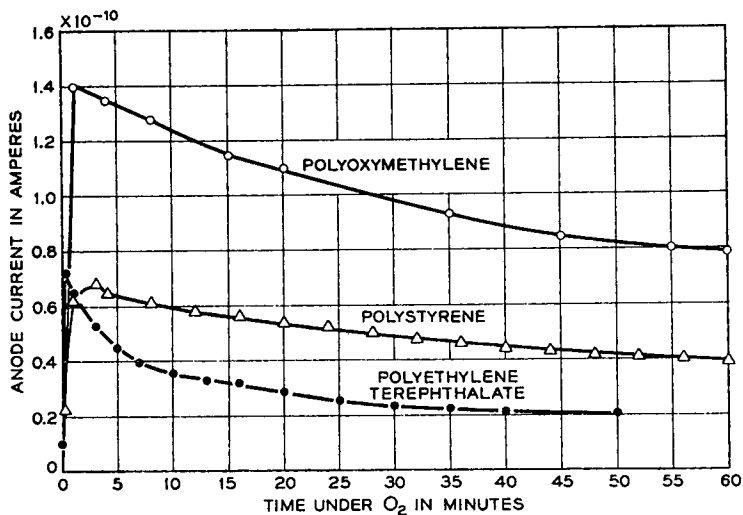


Fig. 2. Oxyluminescence of polymers exhibiting low intensity at 150°C .

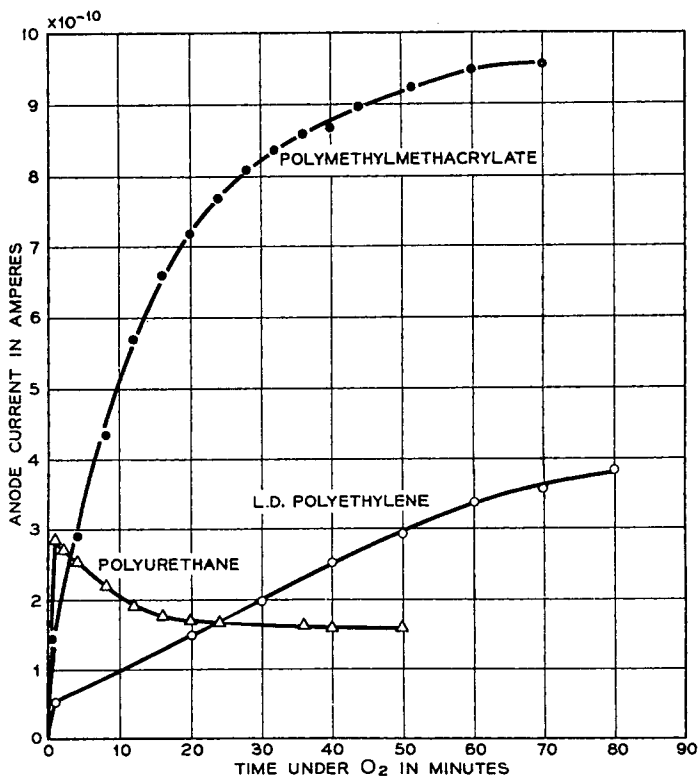


Fig. 3. Oxyluminescence of polymers exhibiting moderate intensity at 150°C .

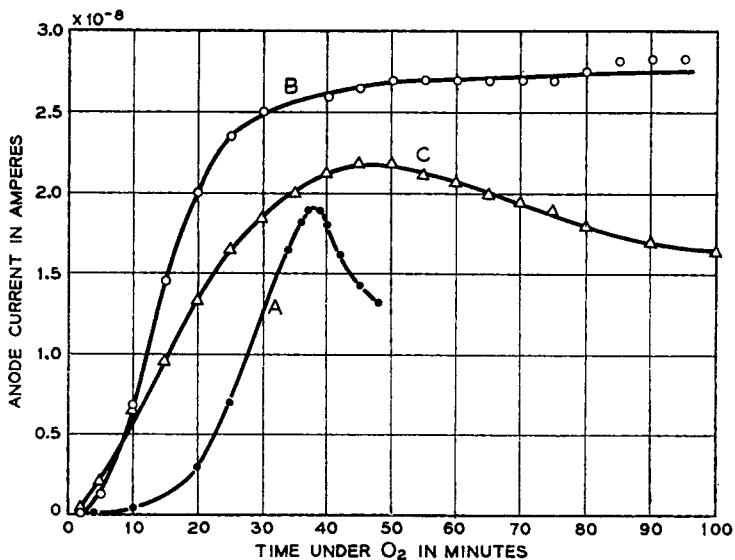


Fig. 4. Oxyluminescence of three commercial unstabilized polypropylenes at 150°C.

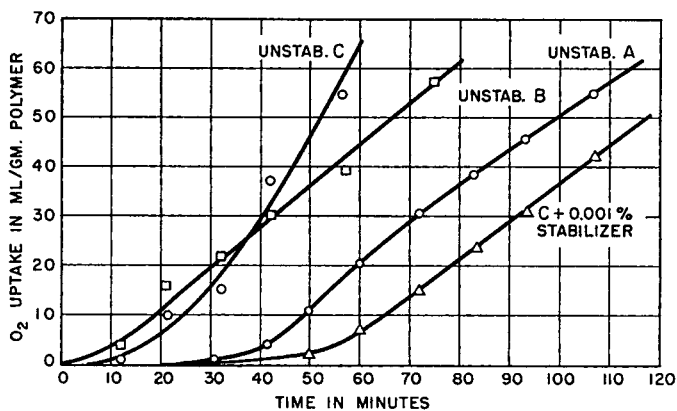


Fig. 5. Oxygen uptake of polypropylenes at 150°C.

exhibiting an intermediate degree of luminosity give curves of different shapes (Fig. 3). The luminosity-time plot for the polyurethane studied resembles the curves obtained with the polymers having lower levels of oxyluminescence. Others, such as low density polyethylene or polymethyl methacrylate show a rather gradual increase in luminosity which appears to approach a steady state condition after an hour or more.

In Figure 4 are shown the curves for three unstabilized commercial polypropylenes which may be classified as strongly oxyluminescent. The shapes of the curves are actually intermediate between those as typified by polyoxymethylene or polyethylene terephthalate and low density poly-

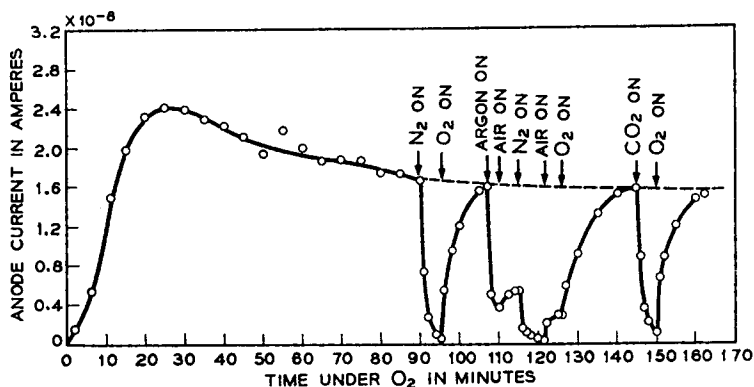


Fig. 6. Effect of various gases on oxyluminescence of unstabilized polypropylene at 155°C.

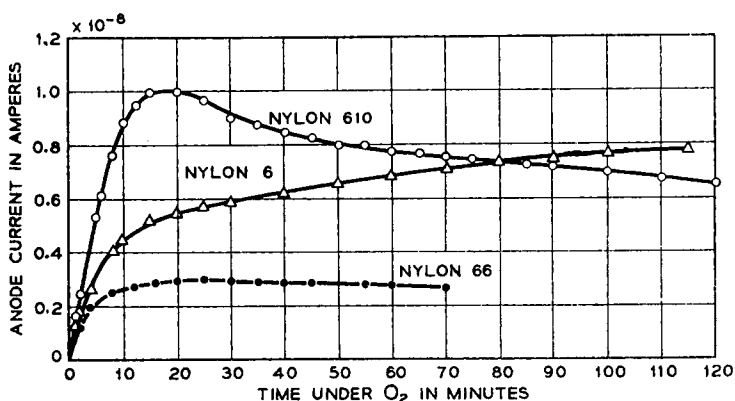


Fig. 7. Oxyluminescence of nylons at 150°C.

ethylene. On adding oxygen to the system, the luminosity increases to a maximum, then decreases and approaches either a steady-state level or a constant rate of decrease apparently due to rapid degradation of the polymer. The reason for the different shapes of the three curves is not at all clear at this time. The three polymers not having stabilizers may have undergone some of the initiating steps of oxidation to different extents, although no fundamental differences in the infrared spectra could be found. Morphological changes may have occurred in the samples after preparation and will be discussed in a subsequent paper. These changes apparently can alter shapes of luminosity-time curves. Polymer A does contain about three times as much ash as the other two and this may be involved in some manner.

The results of oxygen uptake studies on the three polypropylenes are shown in Figure 5. One sees that the three polymers differ in their oxygen absorption characteristics. A had the longest induction period,

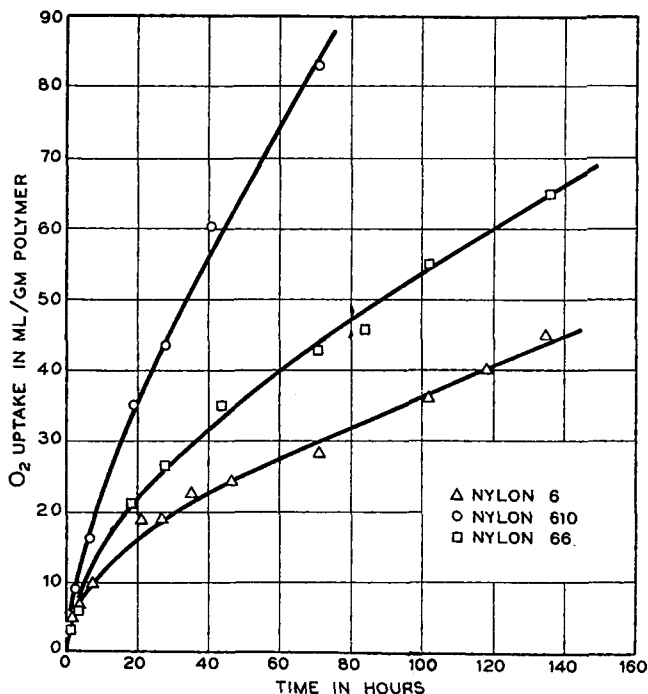


Fig. 8. Oxygen uptake of nylons at 150°C.

37 min. at 150°C.; C had an induction period of 22 min.; while B had only a 5 min. induction time. The luminous intensities showed the inverse order, with A having the lowest value.

It is interesting to observe the build-up or decay of luminescence when the atmosphere of sample is changed. This is shown in Figure 6. After steady-state conditions were reached with the polypropylene sample, the substitution of an inert gas such as nitrogen, argon, or carbon dioxide caused a very rapid loss of luminosity. Renewal of the oxygen resulted in build-up of luminosity over a longer period of time. The build-up and decay appear to involve exponential functions.

Polyamides are also a class of polymers which exhibit strong oxyluminescence. Curves for three different types, nylon 6, nylon 66, and nylon 610 are shown in Figure 7. All of the nylons gave a rapid rise in luminosity on the introduction of oxygen. The curve for nylon 610 shows a noticeable maximum and then falls off and approaches a steady state condition. The luminosity of the nylon 66 increases rapidly to a nearly constant value, about a third that of the 610 polymer. Nylon 6, on the other hand, did not reach a maximum or constant value over the time interval studied. The oxygen uptake curves of these polyamides are shown in Figure 8. They all exhibit an autoretardant characteristic, taking up oxygen with great rapidity at first, and then tapering off. The nylon 610 is noticeably less stable than the nylon 66 or nylon 6, the latter showing the

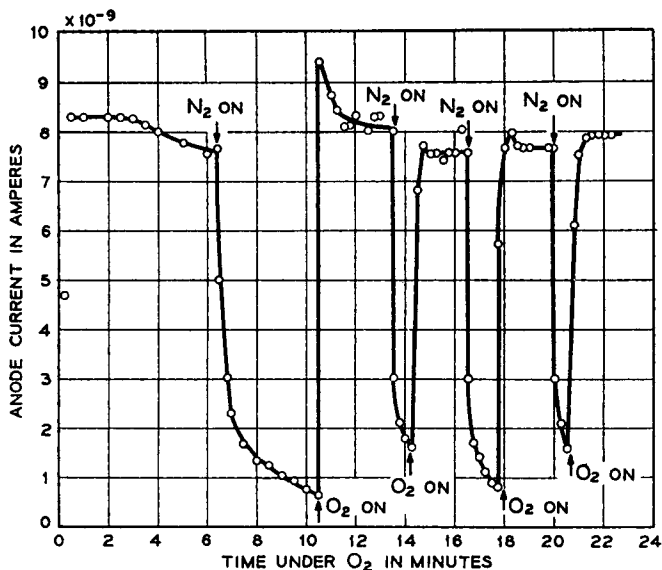


Fig. 9. Effect of nitrogen on oxyluminescence of nylon 6 at 150°C.

most resistance to oxygen. Comparing the oxygen absorption data with the results of the oxyluminescence studies, as summarized in Table I, we see that the lower intensities correspond to the longer t_{10} 's for the case of the nylon 66 and 610. That the nylon 6 is out of line might be explained by the fact that it is somewhat different in nature, being the polyamide of an amino acid, while the other nylons are polyamides of a diamine and dibasic acid.

The effect of alternating oxygen and nitrogen atmosphere on the luminescence of a typical polyamide is illustrated in Figure 9. It appears that the loss of luminosity on substituting nitrogen for oxygen is more rapid than in the case of polypropylene. The intensity in the case of the nylon is reduced to less than 10% of its steady-state value in about 2 min., while a somewhat longer time (4-5 min.) is required for a corresponding reduction in the luminosity of polypropylene. It should, of course, be kept in mind that the time required for complete replacement of oxygen by nitrogen is not accurately known and could be a factor here if too long. One piece of evidence which indicates that this replacement time is actually quite short is the almost instantaneous increase of the luminescence of nylon to the original steady-state value when the nitrogen atmosphere is again replaced by oxygen. Thus, it appears that the formation of the species responsible for the luminosity would appear to be more rapid in the case of the nylon than polypropylene and reaches the equilibrium or steady-state condition much sooner. This could well be in keeping with the auto-retardant character of nylon oxidation, the rapid initial uptake of oxygen corresponding to the rapid build-up of the luminescent species which is

followed by increasing inhibition of the process by the reaction products. In polypropylene this inhibition does not occur but rather further reaction takes place with the active species reacting to give further breakdown products. As a result, the polypropylene approach to equilibrium is more gradual as the growth of the luminescing species is not retarded, but rather they are removed by further reactions at a rate which increases as their concentration increases.

The rapid build-up of luminosity also indicates that the phenomenon occurs principally on the surface of the polymer. Further evidence of this is seen in Table II, which shows no significant differences among samples of the same polymers when the thickness is varied between 7 and 70 mils.

TABLE II
Effect of Thickness on Oxyluminescence (Unstabilized Polypropylene at 150°C.)

Thickness, mil	Steady-state intensity, amp.
7	1.6×10^{-8}
10	2.3×10^{-8}
15	1.9×10^{-8}
70	1.6×10^{-8}

CONCLUSIONS AND SUMMARY

As a result of these studies, one comes to the conclusion that the oxyluminescent effect has much to offer to the study of basic polymer reactions and degradations. It appears that here is a method of studying the reactions and kinetics of a discrete part of the many complicated series of reactions which occur during the oxidative degradation of polymers.

It is also apparent that the intensity of light emitted by polymers when heated in oxygen is dependent upon the nature of polymer. Among polymers of a given general class, the luminosity with respect to time after introduction of oxygen as well as maximum or steady-state intensity may vary with a specific type within the polymer class.

Generally, the intensities of light emission by polymers heated in oxygen reflect their ease of initial oxygen absorption or overall oxidative stability.

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Résumé

La faible émission de lumière par différentes classes et types de polymères lorsqu'ils sont chauffés en présence d'oxygène, l'"oxyluminescence" a été étudiée à l'aide d'un tube photomultiplicateur et d'un microampèremètre sensible. Parmi les polymères à squelette holocarboné les polymères qui ont le plus grand nombre d'atomes de carbone tertiaire montrent généralement une plus grande luminosité. Le polystyrène est une exception notable à cette généralisation. La forme des courbes de luminosité en fonction du temps varie avec le type de polymère. Il a été également trouvé que l'émission de lumière ne cesse pas instantanément quand l'atome d'oxygène est remplacé par un gaz inerte, mais subit plutôt une décroissance exponentielle. La vitesse de décroissance est différente pour les différents types de polymère. Les intensités de luminescence et le temps requis pour atteindre le maximum ou l'état de luminescence constante ont été comparées avec les données de consommation d'oxygène pour différents polymères. En général il existe une corrélation qualitative mais pas nécessairement quantitative entre les intensités lumineuses et les stabilités des polymères en présence d'oxygène.

Zusammenfassung

Die beim Erhitzen verschiedener Polymerklassen und -arten in Sauerstoff auftretende schwache Lichtemission, die "Oxylumineszenz", wurde mittels einer Photomultiplier-Röhre und eines empfindlichen Mikroamperemeters untersucht. Von den Polymeren mit einer Kohlenstoff-Kohlenstoff-Hauptkette zeigten diejenigen mit der grösseren Anzahl tertiärer Kohlenstoffatome in allgemeinen die höheren Lumineszenz-Intensitäten. Eine bemerkenswerte Ausnahme von dieser Verallgemeinerung bildet Polystyrol. Die Form der Helligkeit-Zeit-Kurven war je nach der Art des Polymeren verschieden. Wurde die Sauerstoffatmosphäre durch ein inertes Gas ersetzt, so hörte die Lichtemission nicht sofort auf, sondern klang exponentiell ab. Die Abklinggeschwindigkeit ist offenbar je nach der Art des Polymeren verschieden. Bei verschiedenen Polymeren wurden die Lumineszenz-intensität und die Zeit bis zur Erreichung einer maximalen oder stationären Lumineszenz mit der Sauerstoffaufnahme verglichen; allgemeinen bestand zwar eine qualitative, aber nicht immer eine quantitative Beziehung zwischen der Leuchtintensität und der Polymerstabilität in Gegenwart von Sauerstoff.

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