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CHEMILUMINESCENCE IN THERMO-OXIDATION OF POLYPROPYLENE

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Abstract—Chemiluminescence in thermo-oxidation of polypropylene was interpreted, noting its course with time at different temperatures and the corresponding spectra. The light emission was attributed to decomposition of α-ketone-hydroperoxides and to chain oxidation of polymer proceeding via secondary peroxy radicals.

INTRODUCTION

Chemiluminescence accompanying the thermo-oxidation of polypropylene has been referred to by several authors [1–4]. Reich and Stivala [5] proposed the relationship

$$I_t = k \times \mathrm{ROOH}_t \qquad (1)$$

where k is a constant, according to which luminescence is a function of hydroperoxide concentration; depending on the processes by which hydroperoxides are formed and decomposed, its time course is more or less complicated [6]. The intensity of emitted light depends on the presence of quenchers of excited states in the system and on the concentration of oxygen. Its integral value is also proportional to the concentration of carbonyl groups in polymer. It was found that stationary level of luminescence did not depend on the thickness of the polymer sample in the range 0.018–0.18 mm (ref. [3,4]) confirming that chemiluminescence in the thermo-oxidation of polypropylene is mainly a surface phenomenon. It was also pointed out that values of stationary levels of intensity of luminescence may be useful for judging thermooxidation stability of polymers [1].

Although in the liquid phase oxidation of hydrocarbons the principal process giving out light is disproportionation of secondary peroxy radicals [7], the nature of the reaction steps leading to luminescence in the thermooxidation of solid polymers is uncertain.

In the oxidation of polypropylene, tertiary peroxy radicals predominate as chain carriers; the termination reaction is not exothermic enough to produce observable luminescence. Oxidized polypropylene, however, gives out more marked light emission than polyethylene the oxidation of which proceeds via secondary peroxy radicals.

The kinetic course of chemiluminescence during thermooxidation of polypropylene in both powder and film shows two maxima so far unexplained. Weissman *et al.* [8] suggested that the first maximum is caused by oxidation of the most easily oxidizable centres in the polymer. Several types of peroxidic compounds (hydroperoxides, peroxides, etc.) formed during thermal processing of polymer and decomposing at different rates may also account for the effect.

In the present paper, the changes with time of chemiluminescence during oxidation of isotactic and atactic polypropylene have been investigated under various conditions in an attempt to interpret the light emission during thermo-oxidation of polypropylene.

EXPERIMENTAL

Powdered isotactic polypropylene (Dimitrov Chemical Works, Bratislava) was purified by three fold extraction by boiling *n*-heptane. Films of isotactic polypropylene of thickness 0.5 mm were prepared by pressing the powder in nitrogen at 200°. Powdered atactic polypropylene was oxidized by ozonization and the active oxygen in the polymer was determined iodometrically.

Chemiluminescence measurements were carried out on spectrometer PU SNK 7M made in the Institute of Chemical Physics of the Academy of Sciences of USSR, Moscow. The spectrometer is equipped with photomultiplier FEU-38 (photocathode Sb, Na, K, Cs) with maximum sensitivity at 460 nm. The chemiluminescence spectra were measured using interference filters. The chemiluminescence intensity measured in air or in oxygen was expressed in relative units, one relative unit (rel. u) corresponding to a current of 1.6×10^{-13} A for a circuit resistance of 1×10^{11} Ohm.

RESULTS

Kinetic courses of chemiluminescence intensity in thermooxidation of isotactic polypropylene show 2 maxima (Fig. 1). The first maximum is relatively sharp and is reached in several minutes from the beginning of reaction; its decrease is also quite fast. The intensity, however, does not fall to zero but overlaps the second increase ($I_{\max II}$) which develops relatively slowly and depends markedly on the conditions of experiment.

For atactic polypropylene the intensity of the first maximum decreases with increasing temperature in the range 150–170° (Fig. 2). A similar trend is observed also for polypropylene containing 9×10^{-3} mole kg^{-1} of peroxide groups. The intensity of the second maximum increases with temperature (Table 1). The activation energy, evaluated from the temperature dependence of reciprocal values of time to the first maximum, is 177 kJ mole^{-1}.

For isotactic polymer the chemiluminescence intensity of first maximum increases with temperature; the corresponding Arrhenius plot is not, however, linear.

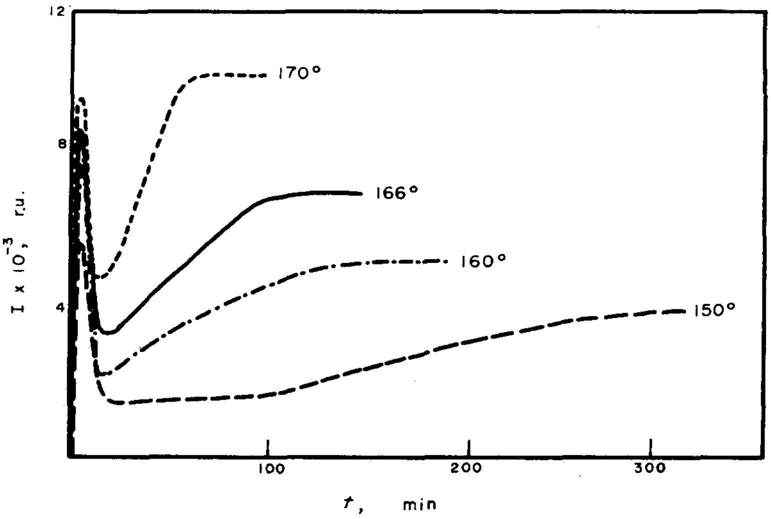


Fig. 1. Time courses of chemiluminescence intensity for films of isotactic polypropylene in the presence of air; temperature range 150–170°.

The activation energy, from the temperature dependence of the second maximum, is 86 kJ mole^{-1}. The value 106 kJ mole^{-1} was obtained from the maximum rate of chemiluminescence increase before the second maximum has been reached (Table 1).

In thermooxidation of films of isotactic polypropylene in oxygen, the first maximum vanishes; the stationary level of chemiluminescence is much higher than for oxidation in air (Fig. 3). The order of dependence of $I_{\max II}$ on the concentration of oxygen is approximately 1.

Films of isotactic polypropylene in nitrogen show only initial increase of luminescence before a fast decrease (Fig. 4). The second maximum does not appear and chemiluminescence intensity remains practically zero. Replacing nitrogen by air or by oxygen leads to the gradual increase of chemiluminescence to its quasi-stationary value $I_{\max II}$. Provided that nitrogen or other inert gas is introduced above the sample throughout the second increase in air, immediate drop of intensity to zero occurs (Fig. 4).

Chemiluminescence intensity of quasi-stationary levels in the second maximum is used for recording of the chemiluminescence spectra in such a way that interference filters of different band transparency are inserted between sample and photomultiplier. The spectrum thus obtained had 3 maxima (Fig. 5) and so it is supposed that during the second increase of luminescence there are at least 3 chemiluminescence processes.

DISCUSSION

The volatile products formed during oxidation of polypropylene (4 hr, 150°, O_2) include about 65% of

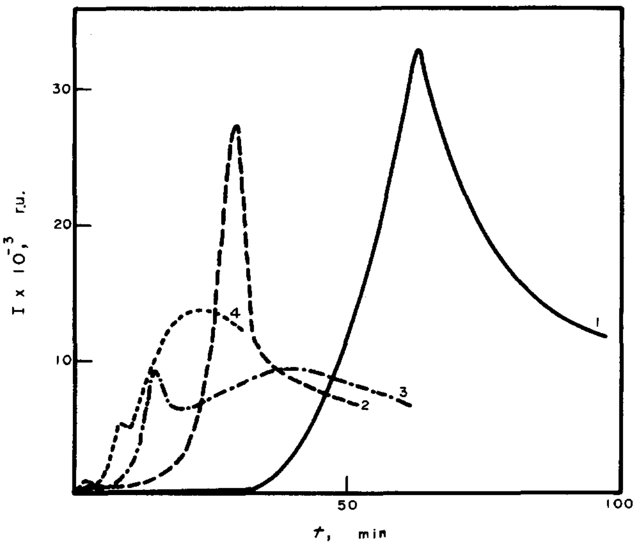
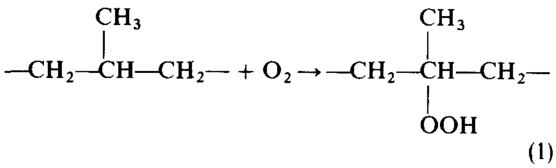


Fig. 2. Time courses of chemiluminescence intensity for powdered atactic polypropylene (weight 50 mg) in air. Temperatures 149.5 (1), 157.0 (2), 162.5 (3) and 167.5° (4).

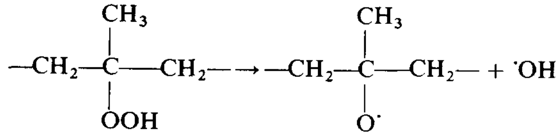
Table 1. Dependence on temperature of the values of chemiluminescence intensity at the first ($I_{\max I}$) and second maximum ($I_{\max II}$) and corresponding times τ_1 of the first maximum. Atactic polypropylene (column A), atactic polypropylene with 9×10^{-3} mole kg^{-1} of peroxides (column B), films of isotactic polypropylene (column C)

	A			B			C		
Temp (°C)	$I_{\max I} \times 10^{-3}$ (rel. u.)	τ_1 (min)	$I_{\max II} \times 10^{-3}$ (rel. u.)	$I_{\max I} \times 10^{-3}$ (rel. u.)	τ_1 (min)	$I_{\max II} \times 10^{-3}$ (rel. u.)	$I_{\max I} \times 10^{-3}$ (rel. u.)	$I_{\max II} \times 10^{-3}$ (rel. u.)	$(dI/dt)_{\max}$ (rel. u./min)
149.4	33.0	62.5							
150.0							5.7	4.0	15.5
151.0				26.2	25.5				
153.1				20.3	18.0				
157.0	27.5	29.0							
157.5				15.2	10.0				
159.5				9.8	5.0				
160.0							7.6	5.1	28.5
161.5				6.2	3.0	4.8			
162.5	9.8	14.5	9.5						
163.0				9.5	3.0	6.0			
166.0							8.6	7.0	46.6
167.5	5.5	8.0	13.8	8.0	2.5	8.8			
169.0				10.8	2.5	12.1			
170.0							9.4	10.1	150.2
174.0	4.4	2.5	13.0						
175.6				13.8	2.5	13.2			

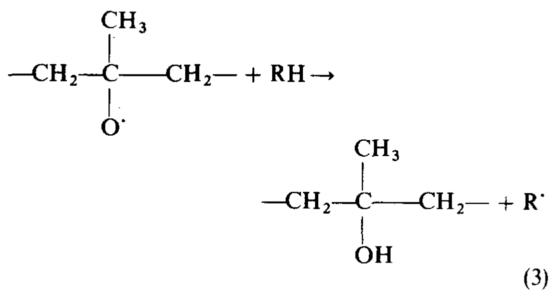
water, 12% of acids, 4% of olefinic compounds, 0.5% of peroxides, 2% of formaldehyde and acetaldehyde, 10% of CO_2, 4% of CO and about 2% of H_2 [9]. The strong dependence of the rate of formation of oxidation products upon peroxide concentration [9] supports the contention that the most of secondary products resulted from the breakdown of tertiary hydroperoxides according to scheme:



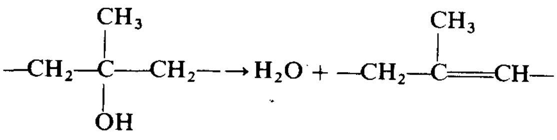
$$-CH_2-\overset{CH_3}{CH}-CH_2- + O_2 \rightarrow -CH_2-\overset{CH_3}{\underset{OOH}{CH}}-CH_2- \quad (1)$$



$$-CH_2-\overset{CH_3}{\underset{OOH}{C}}-CH_2- \rightarrow -CH_2-\overset{CH_3}{\underset{O^{\cdot}}{C}}-CH_2- + {}^{\cdot}OH \quad (2)$$



$$-CH_2-\overset{CH_3}{\underset{O^{\cdot}}{C}}-CH_2- + RH \rightarrow -CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2- + R^{\cdot} \quad (3)$$



$$-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2- \rightarrow H_2O + -CH_2-\overset{CH_3}{C}=CH- \quad (4)$$

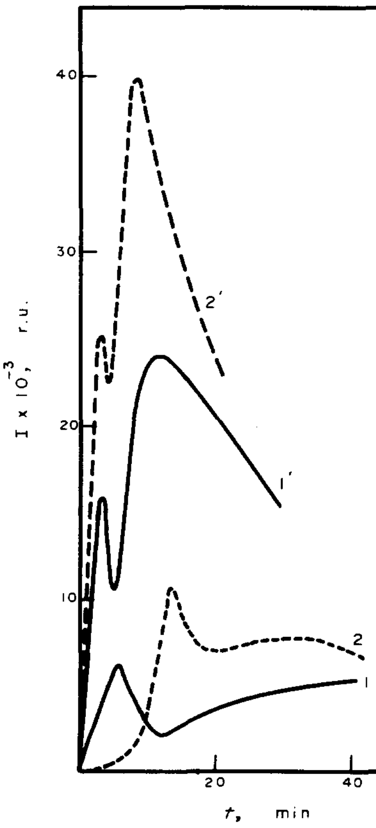


Fig. 3. Time courses of chemiluminescence intensity for isotactic (1,1') and atactic polypropylene (2,2') in air (1,2) and in oxygen (1',2') at 168°. Weight of polymer 50 mg.

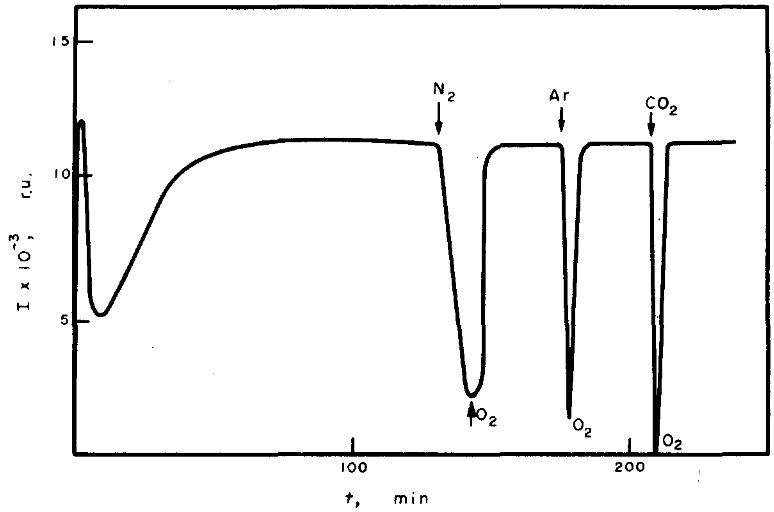
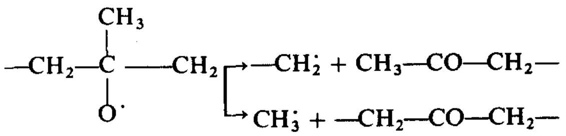


Fig. 4. Time course of chemiluminescence intensity for films of isotactic polypropylene at 170° after introduction of gases above the polymer surface.



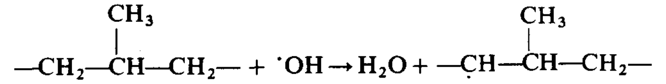
$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O^{\cdot}}{C}}-CH_2\begin{cases}\to -CH_2^{\cdot} + CH_3-CO-CH_2- \\ \to CH_3^{\cdot} + -CH_2-CO-CH_2-\end{cases}\quad (5)$$

$$CH_3^{\cdot} + O_2 \to CH_3O_2^{\cdot} \quad (6)$$

$$-CH_2^{\cdot} + O_2 \to -CH_2O_2^{\cdot}$$

$$2\,CH_3O_2^{\cdot} \to O_2 + 2\,CH_2 = O + H_2 \quad (7)$$

In initiation of oxidation, relatively little attention has been paid to hydroxy radicals which are not very selective in transfer reactions and may react even with methylene groups of polypropylene



$$-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2- + {}^{\cdot}OH \to H_2O + -\underset{\cdot}{C}H-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2- \quad (8)$$

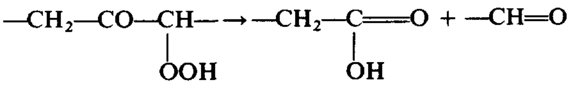
giving with oxygen secondary peroxy radicals. In mutual disproportionation, the latter should emit light due to the excited ketones.

Since the chemiluminescence spectrum shows 3 maxima (Fig. 5), other potential sources of luminescence should be sought. For comparison, the luminescence spectrum of formaldehyde obtained from air oxidation of acetaldehyde and fluorescence spectra of both nontreated sample of polypropylene and the sample oxidized by oxygen are presented (Fig. 5). Unambiguous assignment of particular bands to particular compounds cannot be made because of the complexity of oxidation process. Since only one band with some indication of a shoulder at 460 nm was observed in the fluorescence spectrum of oxidized polypropylene, we may only assume that bands at 460 and 490 nm are due to oxidation reactions in solid polymer whereas that at 390 nm corresponds to reactions above the polymer surface (presumably to the oxidation of either acetaldehyde or formaldehyde).

Since the first increase of chemiluminescence with time was observed even in nitrogen, it is suggested that some peroxidic oxygen is present in polymer before the oxidation as a result of either previous processing or the interaction of chemisorbed oxygen with the polymer surface.

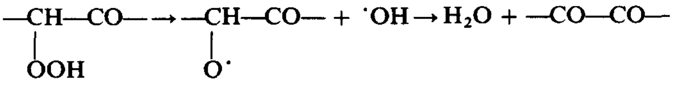
In the triboelectric sequence of polymers, polypropylene behaves as an electron-acceptor. Chemisorption of oxygen may therefore proceed via the superoxide ion-radical which is attached to the polymer surface (RH$^{\cdot}$O$_2^-$). Subsequent reactions of such surface species with oxygen may at ambient temperature yield more oxidized products of polypropylene such as α-ketone-hydroperoxides, α-dicarbonyls etc.

α-Ketone-hydroperoxides decompose into acids and aldehydes [8]



$$-CH_2-CO-\underset{\displaystyle OOH}{\underset{|}{CH}}- \to -CH_2-\underset{\displaystyle OH}{\underset{|}{C}}=O + -CH=O \quad (9)$$

Parallel with reaction (9), there is radical decomposition of α-ketone hydroperoxides



$$-\underset{\displaystyle OOH}{\underset{|}{CH}}-CO- \to -\underset{\displaystyle O^{\cdot}}{\underset{|}{CH}}-CO- + {}^{\cdot}OH \to H_2O + -CO-CO- \quad (10)$$

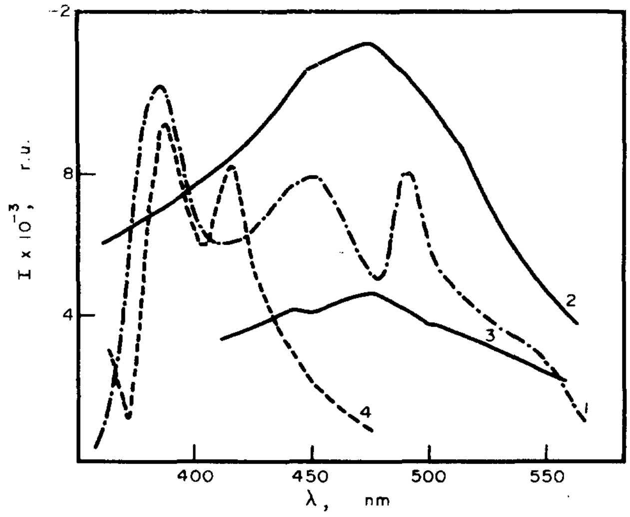


Fig. 5. Chemiluminescence spectrum obtained from values of $I_{\max II}$ (curve 1) compared with fluorescence spectrum of original polypropylene (curve 3) and with that of oxidized isotactic polypropylene (curve 2). Curve 4 represents the fluorescence spectrum of formaldehyde [11].

which involves the disproportionation of α-carbonylalkoxy radicals and hydroxy radicals so that excited α-dicarbonyl compounds are formed.

Decrease in the intensity of the first maximum of chemiluminescence-time courses with temperature for atactic polypropylene may then correspond to a higher activation energy for the rearrangement (9) than for reaction (10). On the other hand, for isotactic polymer where peroxy groups are formed close together [10], β-dicarbonyl sequences are much frequent and rearrangement of hydroperoxides

$$\underset{\displaystyle\text{OOH}}{\text{—CO—}\overset{}{\underset{|}{\text{CH}}}\text{—CO—}}$$

into acids has a lower activation energy than reaction (10). Consequently, the values of chemiluminescence intensity at the first maximum with time increases with rising temperature.

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