Kinetics of Uncatalyzed Thermal Oxidation of Atactic Polybutene-1 by Infrared Spectroscopy

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Synopsis

The uncatalyzed, uninhibited thermal oxidation of a film of atactic polybutene-1 was studied by means of infrared spectroscopy. Reaction temperatures varied from 110 to 130°C. and oxygen concentrations from 12.5 to 100% by volume. A reaction scheme previously reported for the oxidation of isotactic polypropylene was utilized for the atactic polybutene-1. It was found that the scheme and the mathematical expressions derived therefrom could satisfactorily explain the experimental results obtained.

INTRODUCTION

Recently, a scheme was reported which could explain various kinetic results obtained in the uncatalyzed, uninhibited thermal oxidation of isotactic polypropylene (PPr).[1-3] The experimental data were obtained from the quantitative estimation of hydroperoxy and carbonyl groups by infrared spectroscopy[1,2] and from the quantitative estimation of various volatile oxidation products.[3] In this paper, we present an extension of the previously reported mathematical treatment to the case of atactic polybutene-1 (PB). However, the rate of formation of carbonyl groups was studied primarily.

EXPERIMENTAL

Starting Material

An uninhibited PB sample was obtained from Allied Chemical Corporation. This polymer was prepared by the use of Ziegler catalysts and was reported to possess about 98% atactic configuration and to have an approximate weight-average molecular weight of 1.2×10^5. Upon ignition, the ash content was found to be 0.04%. By means of emission spectroscopy, traces of Fe, Al, Si, Na, and Ti were detected.

Apparatus

A Perkin-Elmer recording spectrophotometer, Model 21, was utilized. Attached to this instrument was an oxidation cell which was essentially similar to that previously described.[1]

Procedure

PB films of 2 mil thickness were prepared on sodium chloride disks by slow evaporation of solvent, at reduced temperature, from 5 wt.-% polymer solutions containing n-pentane as solvent. A film sample was placed into the oxidation cell and various dried mixtures of oxygen and nitrogen were passed into the cell at a rate of about 30 cc./min. Pure oxygen and mixtures of oxygen and nitrogen containing 75, 50, 25, and 12.5 vol.-% of the former were used. The reaction temperatures employed ranged from 110 to 130°C. The temperature controller used was sensitive to temperature fluctuations of ±0.1°C. under the experimental conditions employed. By means of infrared spectra, it was ascertained that no pre-oxidation of the sample occurred when the sample was heated to the desired reaction temperature in the presence of a nitrogen atmosphere. Infrared spectra of the carbonyl (5.6–5.8 μ) and hydroxyl (2.8–3.0 μ) regions were recorded at various temperatures and oxygen concentrations as a function of exposure time. The total area of the carbonyl absorbance band was measured by means of a planimeter. The baseline method employed was similar to that previously reported.[1] Plots were constructed of total carbonyl content versus reaction time in order to obtain derived rate data.

RESULTS

As in the case of PPr,[1] it was observed that at all oxygen concentrations employed for PB, the reaction rate increased while the induction period decreased as the reaction temperature was increased. Also, as the oxygen
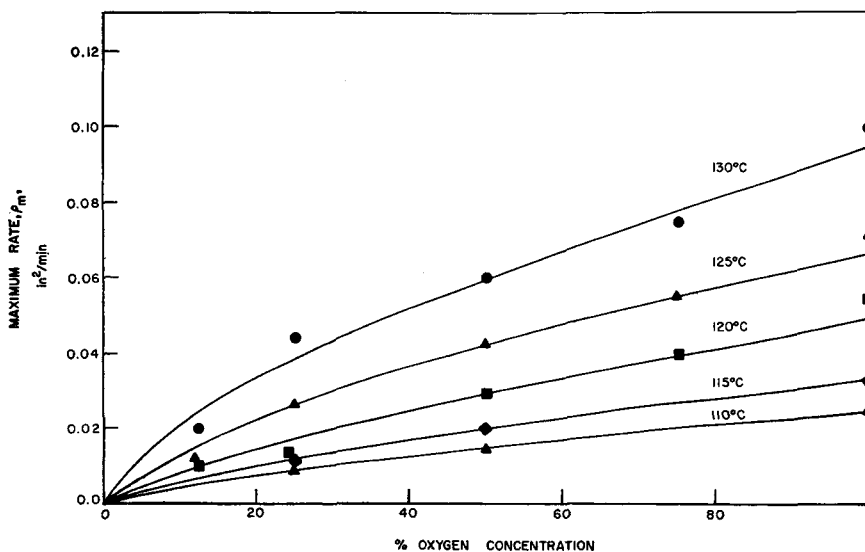

Fig. 1. Plots of maximum rate ρ_m vs. oxygen concentration [O_2] at various temperatures.
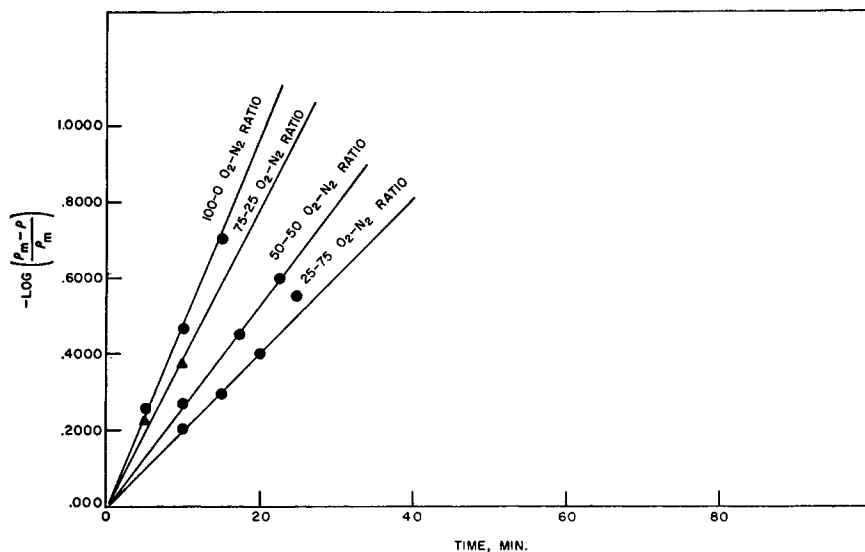
Fig. 2. Plots of $-\log(\rho_m - \rho)/\rho_m$ vs. time.

concentration was increased, the rate of formation of total carbonyl increased while the induction time decreased, at any one given temperature. However, at the same temperature and oxygen concentration, the time required to reach the maximum rate of formation of carbonyl (t_m) was much higher for PB than for PPr.

Maximum rates of formation of total carbonyl (ρ_m) were determined from plots of carbonyl band area versus time for various temperatures and oxygen concentrations. These values are listed in Table 1. Figure 1 has been constructed from the data in Table I and in this figure can be seen curves which appear to possess an initial linear portion at relatively low oxygen concentrations followed by another linear relationship at higher oxygen concentrations.

From Figure 2 can be seen plots of the negative logarithm of the function $(\rho_m - \rho)/\rho_m$ versus exposure time at 130°C. Similar plots were constructed at temperatures in the range of 110–125°C. In all cases, good linear relationships were obtained, as anticipated. (Zero reaction time in these plots was taken at that time when ρ became slightly greater than zero.)

The infrared spectra indicated that the formation of hydroperoxides in the case of PB required a much longer exposure time than for PPr. Also at the higher reaction temperatures used, carbonyl formation was detected much sooner than hydroperoxide formation for PB as compared with PPr.

Weight losses of the PB films used during oxidation due to volatile product formation were determined under various conditions and were found to be generally low.

TABLE I
Maximum Rates of Reaction

Temp., °C.	$10^3/T$, °K.$^{-1}$	Oxygen:nitrogen ratio	Maximum rate, in.^{2}/min.	$\dfrac{\rho_m A \times 10^4}{[O_2]}$
130	2.481	100:0	0.1000	1.00
		75:25	0.0750	0.87
		50:50	0.0600	0.79
		25:75	0.0450	0.83
		12.5:87.5	0.0200	—
125	2.513	100:0	0.0720	0.40
		75:25	0.0300	—
		50:50	0.0421	0.36
		25:75	0.0270	0.43
		12.5:87.5	0.0120	0.40
120	2.544	100:0	0.0550	0.26
		75:25	0.0400	0.24
		50:50	0.0300	0.23
		25:75	0.0130	0.24
		12.5:87.5	0.0100	—
115	2.577	100:0	0.0340	0.14
		75:25	0.0210	—
		50:50	0.0200	0.14
		25:75	0.0120	—
		12.5:87.5	—	—
110	2.611	100:0	0.0260	0.053
		75:25	0.0100	—
		50:50	0.0150	0.053
		25:75	0.0090	—
		12.5:87.5	—	—

DISCUSSION

The reaction scheme and assumptions previously presented for PPr[3] were also employed for PB. The pertinent expressions which were derived are recapitulated in eqs. (1)–(4).

$$\rho_m = \frac{K_1[O_2]}{1 - K_2/(K_3 + [O_2])} \qquad (1)$$

where

$$K_1 = \frac{Ck_4k_3k_6[RH]}{(k_3 + k_4)(k_5 + k_6)} \qquad (1a)$$

and

$C = (1 - e^{-At_m}) \approx$ const., since $At_m \approx$ const. under the experimental conditions employed,

$$K_2 = \frac{2k_3k_5k_8[RH]}{k_9(k_3 + k_4)(k_5 + k_6)} \qquad (1b)$$

$$K_3 = (k_8/k_9)[RH] \qquad (1c)$$

$$\rho_m A / [O_2] = C[RH]k_ik_3k_6/(k_3 + k_4) \qquad (2)$$

$$A' = 1 - K_2/(K_3 + [O_2]) \qquad (3)$$

where

$$A' = A/k' = A/(k_5 + k_6) \qquad (3a)$$

and

$$- \ln (\rho_m - \rho)/\rho_m = At \qquad (4)$$

when $\rho \ll \rho_m$.

For relatively low values of $[O_2]$, eq. (1) becomes,

$$\rho_m = K_1K_3[O_2]/(K_3 - K_2) \qquad (1d)$$

and for relatively high values of $[O_2]$, eq. (1) becomes,

$$\rho_m = K_1K_3 + K_1[O_2] \qquad (1e)$$

From Figure 1, values of K_1, K_2, and K_3 were obtained by means of eqs. (1d) and (1e). Values for these constants are given in Table II for

TABLE II

Comparison of Theoretical Maximum Rates of Reaction with Observed Rates

Temp., °C.	Oxygen: nitrogen ratio	K_1	K_2	K_3	ρ_m, in.^{2}/min. Calculated	Observed
130	100:0	0.00064	33.3	45.5	0.083	0.094
	75:25				0.068	0.078
	50:50				0.050	0.060
	25:75				0.030	0.038
	12.5:87.5				0.017	0.024
125	100:0	0.00047	25.4	38.0	0.058	0.067
	75:25				0.046	0.055
	50:50				0.033	0.043
	25:75				0.020	0.027
	12.5:87.5				0.012	0.015
120	100:0	0.00036	21.2	33.6	0.043	0.050
	75:25				0.035	0.040
	50:50				0.024	0.030
	25:75				0.013	0.017
	12.5:87.5				0.008	0.010
115	100:0	0.00028	14.5	27.0	0.032	0.033
	75:25				0.025	0.027
	50:50				0.017	0.020
	25:75				0.010	0.012
	12.5:87.5				0.006	0.007
110	100:0	0.00024	12.3	24.0	0.025	0.025
	75:25				0.021	0.021
	50:50				0.014	0.015
	25:75				0.008	0.009
	12.5:87.5				0.002	0.005

TABLE III
Values of A', A, and k' for Various Oxygen Concentrations

Temp., °C.	Oxygen: nitrogen ratio	A'		k'	Average k'
		Calculated	Observed		
130	100:0	0.770	0.100	0.130	
	75:25	0.724	0.087	0.120	
	50:50	0.650	0.066	0.105	
	25:75	0.530	0.046	0.087	
	12.5:87.5	0.430	—	—	0.111
125	100:0	0.810	0.055	0.068	
	75:25	0.775	—	—	
	50:50	0.710	0.043	0.060	
	25:75	0.600	0.042	0.070	
	12.5:87.5	0.490	0.041	0.084	0.071
120	100:0	0.840	0.048	0.057	
	75:25	0.800	0.044	0.055	
	50:50	0.770	0.039	0.051	
	25:75	0.690	0.046	0.067	
	12.5:87.5	0.540	—	—	0.057
115	100:0	0.890	0.041	0.046	
	75:25	0.860	—	—	
	50:50	0.810	0.032	0.040	
	25:75	0.720	—	—	
	12.5:87.5	0.630	—	—	0.043
110	100:0	0.990	0.023	0.023	
	75:25	0.880	—	—	
	50:50	0.835	0.018	0.022	
	25:75	0.750	—	—	
	12.5:87.5	0.660	—	—	0.023

various temperatures and oxygen concentrations. From these values, various values of ρ_m were calculated and were found to agree well with observed values (cf. Table II).

Figure 2 illustrates a typical plot of eq. (4) at a particular temperature. From such plots, values of A have been estimated and are listed in Table III. Corresponding values of A' were calculated from eq. (3) and then values of k' were determined from eq. (3a). The values of k' at a given temperature, and for various oxygen concentrations, were approximately constant, as anticipated (cf. Table III).

Arrhenius plots of log K_3 and log (K_2/K_1K_3) were constructed as depicted in Figure 3. From the slopes of the linear relations obtained and from eqs. (1a)–(1c), the following values were obtained: $E_8 - E_9 \approx 10$ kcal./mole and $E_4 + E_6 - E_5 \approx 14$ kcal./mole. From eq. (2), it can be seen that at a given temperature, the value of $\rho_m A/[O_2]$ should be constant for various values of $[O_2]$ (cf. Table I). Furthermore, if it is assumed, as found for PPr,[3] that $k_3 \gg k_4$, then an Arrhenius plot of $\rho_m A/[O_2]$ should yield a value for $(E_4 + E_6)$ (see Fig. 4). This value was found to be about 43 kcal./mole. From this value and preceding values, a value of $E_5 = 29$
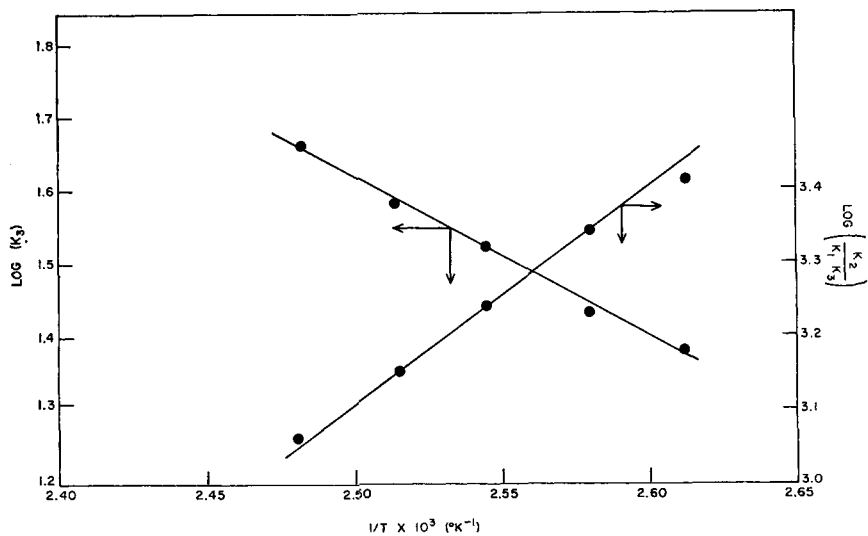
Fig. 3. Plots of log K_3 and log (K_2/K_1K_3) vs. reciprocal temperature, $1/T$.
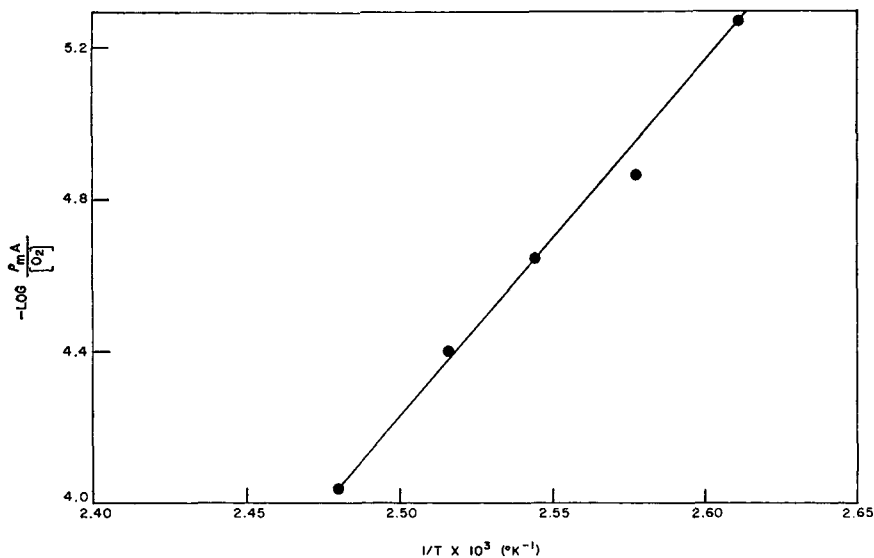

Fig. 4. Plot of $-\log \rho_m A/[O_2]$ vs. reciprocal temperature, $1/T$.

kcal./mole can be calculated. This value agrees well with the value of 30 kcal./mole generally found for the unimolecular decomposition of hydroperoxide.[4] However, it is lower than the value of 33 kcal./mole found for PPr.[3] If it is assumed that $E_4 \approx 30$ kcal./mole,[3,5] then the value of E_6 is 13 kcal./mole. The corresponding value for PPr is 21 kcal./mole.[3] The lower values of E_5 and E_6 for PB as compared with PPr may be related to steric factors. These factors apparently do not play an important role

in the unimolecular decomposition of hydroperoxides to free radicals. Thus, as previously mentioned, a value of E of 30 kcal./mole has been generally found for the unimolecular decomposition of various types of hydroperoxides. However, steric factors may play an important role in the formation of hydroperoxide and in the decomposition of the same into inactive oxidation products. Thus, in the former case, it has been found by means of oxygen absorption measurements that polyisobutylene (PIB) is less readily attacked by oxygen than PPr.[6] Also, we have observed that PIB behaves similarly to PB during oxidation, in that they both require much longer exposure times than PPr before hydroperoxides can be detected by infrared spectroscopy.[7] Thus, it would appear that the value of E_i assumed for PB should probably be greater (the value of E_6 would consequently be lower). Assuming that the value of E_i for PB is larger than that for PPr, then the values of E_i and E_6 for PB could indicate that hydroperoxide formation (based upon the initiation step) for PB should be slower than for PPr, whereas, hydroperoxide decomposition into inactive oxidation products (step 6)[1] should occur more rapidly for PB than for PPr. (Values of k' of PB are also much higher than corresponding values for PPr at a given temperature.) Under the preceding conditions, it would be anticipated that longer exposure times would be required for the detection of the hydroperoxide moiety in the case of PB. Although the transient hydroperoxide moiety in the PB film may not be detectable by infrared during the early exposure times, the carbonyl moieties can nevertheless be forming at such a rate that they can be detected by infrared.

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Résumé

On a étudié par spectroscopie infrarouge l'oxydation thermique non catalysée et non inhibée d'un film de polubutene-1 atactique. Les températures de réaction variaient de 110 à 130°C et les concentrations en oxygène de 12.5 à 100% en volume. Un schéma de réactions décrit antérieurement pour l'oxydation du polypropylene isotactique a été employé dans le cas du polybutene-1 atactique. On a trouvé que le schéma obtenu et les expressions mathématiques qui en découlent peuvent expliquer d'une façon satisfaisante les résultats expérimentaux obtenus.

Zusammenfassung

Die unkatalysierte, nicht inhibierte thermische Oxydation eines Films aus ataktischem Polybuten-1 wurde infrarotspektroskopisch untersucht. Die Reaktionstemperaturen variierten von 110–130°C und die Sauerstoffkonzentration von 12.5 bis 100 Volumsprozent. Ein früher für die Oxydation von isotaktischem Polypropylen aufgestelltes Reaktionsschema wurde für das ataktische Polybuten-1 benützt. Es zeigte sich, dass das Schema und die daraus abgeleiteten mathematischen Ausdrüke die Versuchsergebnisse befriedigend erklären könnten.