Kinetics of the thermal oxidation of poly(4-methyl-1-pentene) from volatile products using thermogravimetric analysis

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The kinetics of the thermal oxidation of isotactic poly(4-methyl-1-pentane) were studied in the bulk phase using thermogravimetric analysis (t.g.a.) at temperatures from 155° to 185°C and oxygen concentration from 75 to 100% by volume. The kinetics derived from formation of volatile products using t.g.a. correspond to those from non-volatile carbonyl products obtained from infra-red spectrometry.

INTRODUCTION

The kinetics of the thermal oxidation of atactic and isotactic forms of polypropylene (PP) and poly(1-butene) (PB) in the bulk phase have been reported by Stivala, Reich, and coworkers[1,2] in the absence of additives and in the presence of metal salts. These workers proposed a general mechanism from rate of carbonyl formation at various temperatures and oxygen concentrations observed from infra-red (i.r.) spectra. Recently, Gabbay and Stivala have extended these studies to isotactic poly(1-pentene) (PP-1)[3], and atactic and isotactic poly(4-methyl-1-pentene) (IPMP)[4] and found that the general kinetic scheme was applicable to these polymers. However, at temperatures exceeding about 145°C, corrections to the measured areas of the i.r. carbonyl bands for the IPMP were necessary in order to account for high loss of volatile carbonyl products. The general kinetic scheme was originally based on non-volatile carbonyl product formation for the case where volatile loss is small (less than about 3%).

The purpose of this paper is to confirm the kinetic scheme for IPMP by observing the formation of volatile products using thermogravimetric analysis (t.g.a.).

EXPERIMENTAL

Apparatus

A Du Pont thermogravimetric analyzer Model 95 was used to record the weight losses of the IPMP films as a function of time at different temperatures and oxygen concentrations.

Procedure

Films of IPMP prepared and used in an earlier study[4] were used in the t.g.a. to record weight losses as a function of time, under 100% O_2, 87.5% O_2 and 75% O_2 in the temperature range of 125° to 185°C. The isothermal mode was used in the t.g.a. with rate of flow of gases (O_2/N_2) sweeping the sample maintained at 30 cm^3/min. The conditions of temperature, oxygen concentration, sample size and rate of gas flow were identical to those used in the earlier study in obtaining rate of carbonyl formation from i.r. spectra.

RESULTS

Table 1 summarizes the weight percent of volatile products

Table 1 Weight losses of isotactic poly(4-methyl-1-pentene) oxidized at different temperatures and oxygen concentrations using t.g.a.

Temperature (°C)	Time (min)	Percentage weight loss 100% O_2	87.5% O_2	75% O_2
185	3	2.8	2.5	2.0
	6	6.0	5.0	4.0
	9	9.5	8.5	6.0
	12	12.8	10.5	7.5
	15	16.0	13.0	9.0
175	5	2.0	1.5	1.2
	10	4.0	3.4	3.0
	15	6.0	5.0	4.0
	20	8.0	6.5	6.0
	25	10.0	8.0	7.0
	30	12.0	10.0	8.5
	35	13.0	11.5	10.0
165	5	1.5	1.0	–
	10	3.0	2.0	1.5
	15	4.2	3.2	2.5
	18	5.0	–	–
	24	6.8	5.5	4.0
	27	7.8	–	–
	30	8.5	6.5	4.5
	35	10.0	7.5	5.5
155	5	0.9	0.5	0.3
	10	1.5	–	–
	15	2.5	1.5	1.0
	20	3.0	2.0	1.2
	25	4.0	2.5	1.5
	30	4.5	3.0	2.0
	35	5.5	3.5	2.2
	40	6.0	4.0	2.5
145	120	3.0	–	–
140	120	2.8	–	–
125	120	2.5	–	–

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formed during the reaction at the conditions indicated. No appreciable volatile products are formed at temperatures below 155°C. *Figure 1* shows that the plot of ln $(1-w)^{-1}$ against time t at 155°C, where w is weight fraction of volatiles, is linear, indicating that the rate of volatile product formation obeys first-order kinetics. *Table 2* contains the rate of volatile product formation from t.g.a. obtained from plots similar to *Figure 1*.

DISCUSSION

The general kinetic scheme for the thermal oxidation of polyolefins[1,2] was reproduced in a recent paper[3] on PP-1, and the same kinetic parameters are used in this paper except the parameter d*VP*/d*t* derived in this paper.

The rate of formation of volatile products as indicated in step 7 of the general kinetic scheme, where RO· radicals decompose to form the volatile products, VP, and R· radicals is:

$$\frac{\mathrm{d[VP]}}{\mathrm{d}t} = k_7[\mathrm{RO\cdot}] \qquad (1)$$

Applying the steady-state approximations:

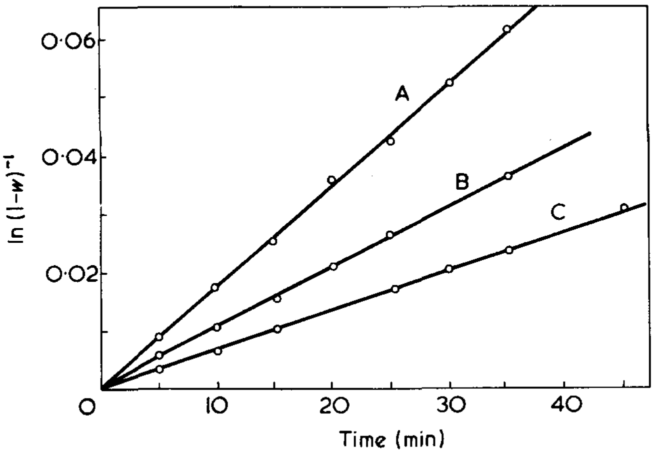

Figure 1 Plot of ln$(1-w)^{-1}$ vs. time of isotactic poly(4-methyl-1-pentene) oxidized at 155°C as a function of $[O_2]$. A, 100% O_2; B, 87.5% O_2; C, 75% O_2

$$\frac{\mathrm{d[RO\cdot]}}{\mathrm{d}t} = 2k_5[\mathrm{RO_2R}] - k_7[\mathrm{RO\cdot}] = 0 \qquad (2)$$

$$[\mathrm{RO\cdot}] = \frac{2k_5}{k_7}[\mathrm{RO_2R}] \qquad (3)$$

where

$$[\mathrm{RO_2R}] = \frac{k_1k_3[\mathrm{RH}]\,(1-e^{-At})\,[O_2]}{(k_3+k_4)A} \qquad (4)$$

From equations (3), (4), and equation (1):

$$\frac{\mathrm{d[VP]}}{\mathrm{d}t} = \frac{2k_5\cdot k_1k_3[\mathrm{RH}]\,(1-e^{-At})\,[O_2]}{(k_3+k_4)A} = C[O_2] \qquad (5)$$

where A and C are constants under given set of conditions and RH its polymer.

From expressions previously reported by Stivala and Reich, the maximum rate of carbonyl formation, ρ_m, can be expressed as:

$$\rho_m = \frac{k_6\cdot k_1k_3[\mathrm{RH}]\,(1-e^{-t_m})\cdot[O_2]}{(k_3+k_4)A} \qquad (6)$$

where t_m is time to reach ρ_m. Hence, from equation (5) and (6):

$$\frac{\mathrm{d(VP)}}{\mathrm{d}t} = \rho_m\frac{2k_5}{k_6} \qquad (7)$$

Equation (5) corresponds to a linear relationship between d[VP]/dt and $[O_2]$ providing [RH] and e^{-At} remain unchanged with varying $[O_2]$[1,2] and this is confirmed in *Figure 2*. Further, equation (7) holds providing $e^{-At} \approx e^{-At_m}$, which may be reasonable at high temperatures and $[O_2]$. This may be confirmed by comparing values of $(\mathrm{d[VP]}/\mathrm{d}t)_{\mathrm{t.g.a.}}$ to those of $(2k_5\rho_m/k_6)_{\mathrm{i.r.}}$. Accordingly, values of k_5, k_6 and ρ_m determined from the non-volatile carbonyl products using i.r. from previous studies[4–6], were used to obtain values of $(2k_5\rho_m/k_6)_{\mathrm{i.r.}}$ (see *Table 2*). Values of $(\mathrm{d[VP]}/\mathrm{d}t)_{\mathrm{t.g.a.}}$ obtained using t.g.a., agree reasonably

Table 2 Kinetic parameter of isotactic poly(4-methyl-1-pentene) oxidized above 150°C

Temperature (°C)	$(k_5 \times 10^9)^\dagger$	$(k_6 \times 10^6)^\dagger$	$[O_2]$ (%)	$\rho_m{}^\dagger$	$\frac{2k_5\rho_m}{k_6}$	$(\mathrm{d[VP]}/\mathrm{d}t)_{\mathrm{t.g.a.}}{}^\ddagger$
155	0.20	0.147	100	0.560	0.0015	0.0013
			87.5	0.520	0.0010	0.0010
			75	0.480	0.0013	0.0009
165	0.30	0.208	100	0.780	0.0022	0.0028
			87.5	0.730	0.0021	0.0023
			75	0.690	0.0019	0.0022
175	0.70	0.366	100	1.030	0.0039	0.0044
			87.5	0.961	0.0036	0.0038
			75	0.900	0.0034	0.0030
185	1.20	0.428	100	1.420	0.0080	0.0108
			87.5	1.340	0.0075	0.0095
			75	1.260	0.0070	0.0080

† From i.r. data of non-volatile products[4]. ‡ From t.g.a. data in this study, of volatile products

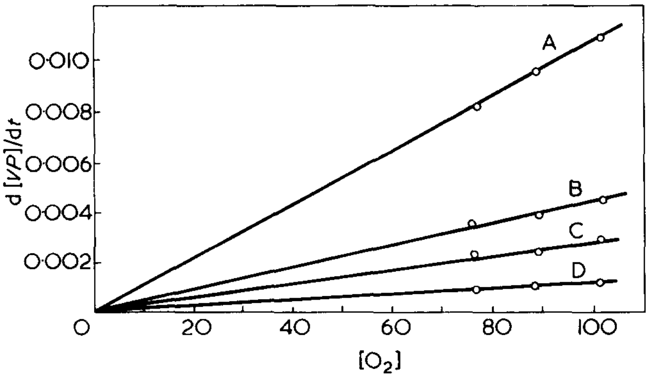

Figure 2 Plot of rate of volatile product (*VP*) formation vs. $[O_2]$ of isotactic poly(4-methyl-1-pentene) as a function of temperature using t.g.a. A, 185°C; B, 175°C; C, 165°C; D, 155°C

well with $(2k_5\rho_m/k_6)_{i.r.}$, (*Table 2*). These observations support the general kinetic scheme reported by Stivala and Reich. It should be mentioned that the kinetic parameter A obtained by i.r. (from the general kinetic scheme) compared favourably with that obtained by other methods, such as O_2 absorption and oxyluminescence, from both non-volatile and volatile products of oxidation[2].

The higher weight loss at 155°C and above (*Table 1*) is due to attack on the tertiary carbon of the pendant groups in the IPMP. The data in *Table 1* were used in the earlier study[4] on this polymer to correct the i.r. data due to some loss of the volatile carbonyl compounds. Arrhenius plots of the kinetic data[4] from 125° to 185°C produced two linear curves, intersecting at 155°C. The point of intersection occurs at the temperature where significant volatiles are beginning to form, corresponding to small fragments from cleavage of the tertiary carbons on the pendant groups.

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