

Kinetics of Autoxidation of Isotactic Polybutene-1 by Infrared Spectroscopy

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Synopsis

The autoxidation of a film of isotactic polybutene-1 (IPB) containing a relatively large amount of metallic ash ($\approx 0.2\%$) was studied by means of infrared spectroscopy. Reaction temperatures were varied from 105 to 120°C and oxygen concentrations from 25 to 100% by volume. A reaction scheme previously reported for the autoxidation of atactic polybutene-1 (APB) was utilized for the IPB. Various results obtained for IPB were compared with those previously reported for APB.

Introduction

Recently, a scheme was reported which could explain various kinetic results obtained in the uncatalyzed, uninhibited thermal oxidation of atactic polybutene-1 (APB)¹ and isotactic polypropylene (PPr).²⁻⁴ In this paper, we present an extension of the previously reported mathematical treatment to the case of isotactic polybutene-1 (IPB). The experimental data were obtained from the quantitative estimation of carbonyl groups by infrared spectroscopy.^{1,4}

EXPERIMENTAL

Starting Material

An uninhibited IPB sample was obtained from the Allied Chemical Corp. through the courtesy of Dr. C. D. Mason. This polymer, prepared by the use of Ziegler catalysts, was reported to have an approximate weight-average molecular weight of 1×10^6 and to possess >90% isotactic configuration. The IPB films used in this study were prepared by dissolving purified IPB in carbon tetrachloride from which films (ca. 2-3 mil) were cast on sodium chloride disks. The films were allowed to air dry at room temperature and were presumably of Form III.⁵ Upon ignition, the ash content was found to be 0.17%. The ash contained mainly Al, Ti, and Si, with lesser amounts of Mg, Pb, Fe, Ca, Mn, Sn, and Cu, assessed from emission spectroscopy.

Apparatus

A Perkin-Elmer recording spectrophotometer, Model 21, was used. Attached to this instrument was an oxidation cell which was essentially similar to that previously described.⁴

Procedure

The unpurified IPB (ca. 0.4% ash) was extracted with iso-octane at reflux temperature and after filtration, the solution was cooled and the precipitated IPB collected. This procedure was reported several times to afford purified material having an ash content of 0.17%. This material was dissolved in carbon tetrachloride and some of the resulting solution was poured in a mold containing a base consisting of a sodium chloride disk. IPB films of 2¹/₂ mil thickness were obtained by slow evaporation of solvent at room temperature. The resulting film and sodium chloride disk were air-dried, stored under vacuum and later placed into the oxidation cell. 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, and 25 vol-% of the former were used. The reaction temperature employed ranged from 105 to 120°C. The temperature controller was sensitive to temperature fluctuations of $\pm 0.1^\circ\text{C}$ under the experimental conditions used. 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 nitrogen. Infrared spectra of the carbonyl (5.6–5.8 μ) region 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 a planimeter using a baseline method similar to that previously reported.¹ Plots were constructed of total carbonyl content vs. reaction time to obtain derived rate data.

Results

As in the cases of PPr⁴ and APB,¹ it was observed that for the IPB, at all oxygen concentrations employed, the reaction rate increased while the induction period decreased with increasing reaction temperature. Further, as the oxygen concentration was increased, the rate of formation of total carbonyl increased while the induction time decreased, at any one given

TABLE I
Comparison Between Induction Times, θ , for APB and IPB

Temperature, °C	[O ₂], vol-%	θ_{APB} , min	θ_{IPB} , min
110	50	495	45
110	75	405	30
110	100	195	30
115	50	285	40
115	75	225	15

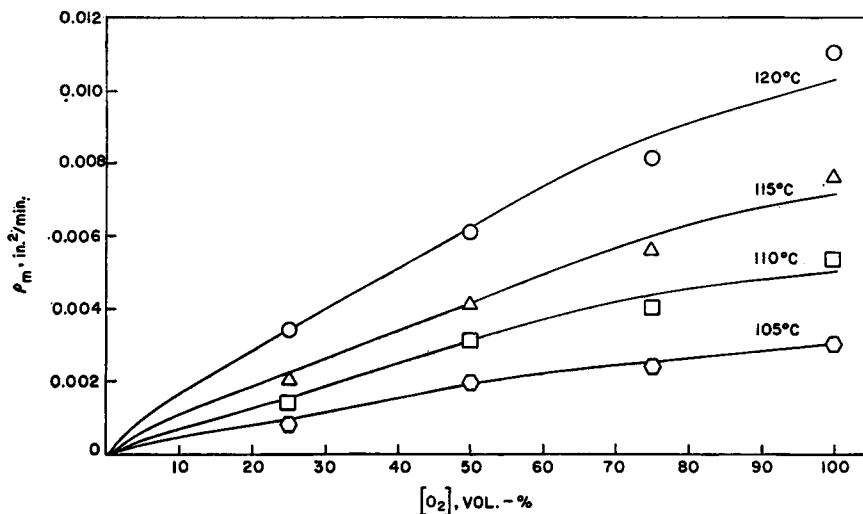


Fig. 1. Plots of maximum rate ρ_m versus oxygen concentration $[\text{O}_2]$ at various temperature.

temperature. However, at the same temperature and oxygen concentration, the induction time (θ) for APB was much higher than that for IPB (cf. Table I).

Maximum rates of formation of total carbonyl (ρ_m) were determined from plots of carbonyl band area vs. time for various temperatures and oxygen concentrations. These values are listed in Table II. Figure 1 has been constructed from the data in Table II.

TABLE II
Comparison of Theoretical with Observed Maximum Rates

Temp., °C	$[\text{O}_2]$, vol.-%	$K_1 \times 10^6$	K_2	K_3	ρ_m , $\text{in.}^2/\text{min}$	
					Calcd.	Obsd.
105	25	1.8	50	60	0.0011	0.0008
	50				0.0017	0.0020
	75				0.0022	0.0024
	100				0.0026	0.0030
110	25	2.8	65	80	0.0018	0.0014
	50				0.0028	0.0031
	75				0.0037	0.0040
	100				0.0045	0.0053
115	25	3.5	85	100	0.0027	0.0021
	50				0.0041	0.0041
	75				0.0052	0.0056
	100				0.0062	0.0076
120	25	4.6	115	125	0.0049	0.0034
	50				0.0067	0.0061
	75				0.0081	0.0081
	100				0.0094	0.011

Weight losses of the IPB films during oxidation, due to volatile product formation, were determined under various conditions and were found to be generally low after many hours of reaction time. Thus, e.g., after ca. 7 hr at 115°C, using pure oxygen, the weight loss was less than 1%.

Discussion

The reaction scheme and assumptions previously presented for PPr⁴ were also employed for IPB. The pertinent expressions which were derived are recapitulated in eqs. (1)–(4).

$$\rho_m = \frac{K_1[\text{O}_2]}{1 - K_2/(K_3 + [\text{O}_2])} \quad (1)$$

where

$$K_1 = \frac{Ck_4k_5k_6[\text{RH}]}{(k_3 + k_4)(k_5 + k_6)} \quad (1a)$$

and, $C = (1 - e^{-At_m}) \approx \text{const.}$, since $At_m \approx \text{constant}$ under the experimental conditions employed (1.6 ± 0.2 over the temperature range of 105–120°C),

$$K_2 = \frac{2k_3k_5k_6[\text{RH}]}{k_9(k_3 + k_4)(k_5 + k_6)} \quad (1b)$$

$$K_3 = (k_3/k_9) [\text{RH}] \quad (1c)$$

$$k_5 = (k_4/k_3)k'K_2/K_3 \quad (2)$$

$$A' = 1 - K_2/(K_3 + [\text{O}_2]) \quad (3)$$

where

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

and

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

when $\rho \ll \rho_m$.

For relatively low values of $[\text{O}_2]$, eq. (1) becomes,

$$\rho_m = K_1K_3[\text{O}_2]/(K_3 - K_2) \quad (1d)$$

and for relatively high values of $[\text{O}_2]$, eq. (1) becomes,

$$\rho_m = K_1K_3 + K_1[\text{O}_2] \quad (1e)$$

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 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). Values of K_2 were obtained using eq. (1d) and arbitrarily drawing initial slopes in Figure 1 such that the values obtained

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

Temp., °C	[O ₂], vol-%	A'	A	k'_{IPB} , min ⁻¹	k'_{APB} , min ⁻¹
105	50	0.55	0.018	0.032	—
	75	0.63	0.023	0.036	—
110	50	0.50	0.023	0.046	0.022
	75	0.58	0.030	0.052	—
	100	0.64	0.039	0.060	0.023
115	50	0.43	0.030	0.070	0.040
	75	0.51	0.039	0.076	—
120	50	0.34	0.037	0.11	0.051

would give best fit with experimental points. From eq. (4), values of A were estimated at various temperatures and oxygen concentrations and are

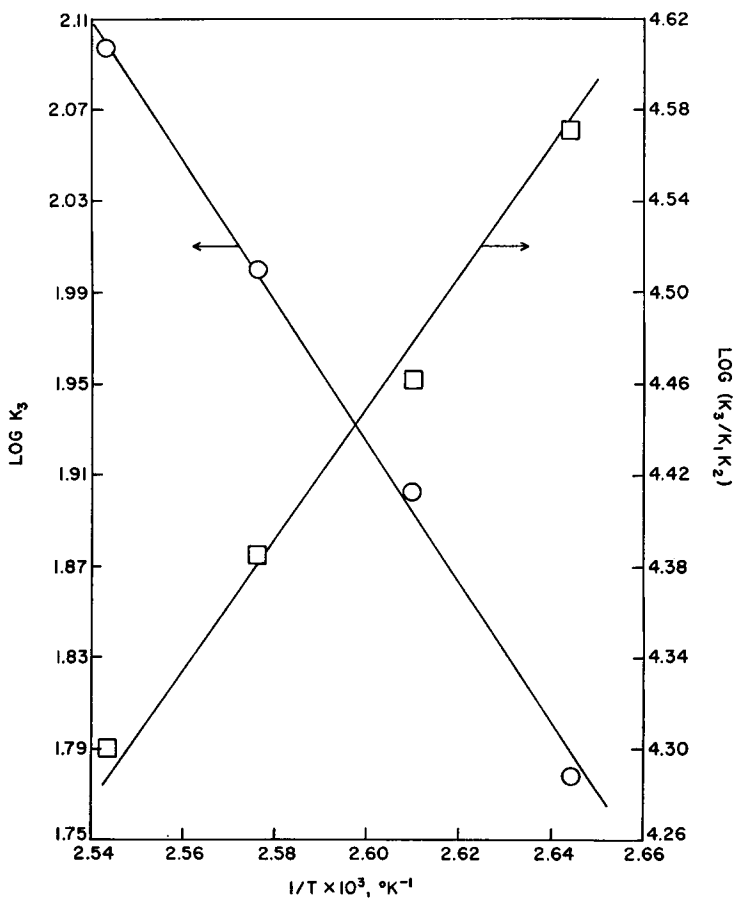


Fig. 2. Plots of $\log K_3$ and $\log (K_2/K_1K_2)$ versus reciprocal temperature, $1/T$.

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 2. From the slopes of the linear relations obtained and from eqs. (1a)–(1c), the following values were obtained: $E_3 - E_9 \approx 14$ kcal/mole and $E_4 + E_6 - E_5 \approx 13$ kcal/mole. From eq. (2), it can also be seen that

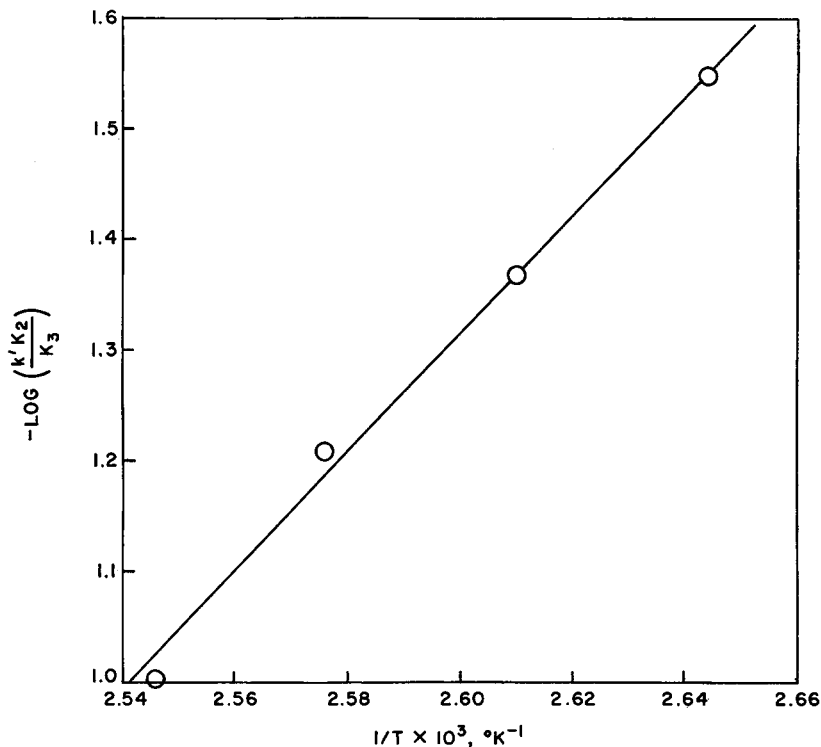


Fig. 3. Plot of $-\log (k' K_2/K_3)$ versus reciprocal temperature, $1/T$.

if (k_4/k_3) is constant over the temperature range utilized (this was previously reported to be approximately true for APB^6), then an Arrhenius plot of $\log (k'K_2/K_3)$ should afford a value of E_5 . In this manner, $E_5 \approx 25$ kcal/mole (cf. Fig. 3). Utilizing this latter value, $E_4 + E_6 \approx 38$ kcal/mole. For APB^1 , it was found that $E_5 = 29$ kcal/mole, $E_4 + E_6 = 43$ kcal/mole, and the values of k' for APB^1 were approximately one-half those for IPB at the same temperature (cf. Table III).

The above data plus the data in Table I indicate that various autoxidation processes are occurring more rapidly for IPB than for APB under similar experimental conditions. At first thought, it would appear unusual

for a stereotactic (and more crystalline) polybutene-1 to undergo autoxidation more readily than an atactic polybutene-1 in view of data obtained for polypropylene.⁷ However, it has been reported that the crystalline regions of poly (3-methyl-1-butene) were readily oxidized along with the amorphous regions.⁷ Thus, one might expect that the activation energies for various autoxidation processes occurring during the oxidation of APB and IPB could be similar. However, as previously indicated, IPB appears to undergo autoxidation more readily than APB in view of the shorter induction times, the larger values of k' , and the lower values of activation energy for the former polymer. We tentatively attribute such behavior to the presence of much larger amounts of metallic impurities in IPB (0.17% as ash) than in APB (0.04% as ash). Thus, Ryshavy and Balaban⁸ studied the effect of residues of the Ziegler catalyst type upon the degradation rate of isotactic polypropylene. When this polymer, containing TiCl_3 and $(\text{Et})_3\text{Al}$, was subjected to the action of air at 200°C at various times and dried in vacuum at 60°C, there were marked changes in viscosity as a function of reaction time and ash content. Furthermore, it is well known that metal salts can act as accelerators of hydrocarbon oxidation⁹ and can lower the activation energy value for hydroperoxide decomposition (E_5). Thus, Lombard and Knopf¹⁰ found that the cobaltic acetyl-acetonate catalyzed decomposition of cumene-hydroperoxide in solution afforded a value of $E_5 = 25$ kcal/mole, whereas in the absence of the metal salt, a value of $E_5 = 31$ kcal/mole was obtained. Recently, Osawa, Shibamiya, and Matsuzaki¹¹ reported on the thermal oxidative degradation of polypropylene catalyzed by metallic salts of fatty acids. They found that the addition of 0.5 wt-% of fatty acid salts of transition metals, e.g., titanium (IV) stearate, to finely powdered polypropylene lowered the induction time of the pure polymer from about 125 to about 30 min based on oxygen absorption studies at 125°C. Furthermore, some metallic salts, e.g., cupric stearate, were capable of lowering an "apparent" activation energy of the autoxidation from 30 for the pure polymer to about 24 kcal/mole for the metal-containing polypropylene.

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