# Molecular Weight Changes During Polyolefin Autoxidation

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## Synopsis

Expressions were derived relating changes of intrinsic viscosity to reaction time, based on a scheme previously presented for the uncatalyzed, uninhibited thermal oxidation of polyolefins. A value of the kinetic parameter $A$ may be obtained from these expressions by using an iterative type of procedure and employing data presented by other workers for the oxidation of atactic polybutene-1. This value of $A$ was compared with the corresponding value obtained by the authors from rate of carbonyl formation studies in oxidation of atactic polybutene-1 by means of infrared absorption spectroscopy methods. The good agreement between the values of $A$ obtained from the two different experimental techniques employed lends further support to the validity of the scheme used and the expressions derived therefrom.

## Introduction

The authors have previously presented a scheme for polyolefin autoxidation which was applied to isotactic polypropylene[1-5] and atactic polybutene-1[5,6] in the absence of additives. The thermal oxidation kinetics of films of these polyolefins were studied by using infrared spectroscopy, as a function of temperature and oxygen-to-nitrogen ratios, by observing rates of carbonyl and hydroperoxide formation. Activation energies were estimated for various steps in the scheme along with various other kinetic parameters, e.g., $A$. It was found that when the parameter $A$ was calculated either from rates of carbonyl or from rates of hydroperoxide formation, by optical methods, the agreement between the values of $A$ obtained was very good.[1,2] This parameter was also calculated from data reported by other investigators for polypropylene oxidation which involved studies of rate of formation of volatile products[3,5,7,8] of chemiluminescence[4,9,10] and of oxygen absorption,[4,9,10] Generally speaking, values of $A$ obtained from these various experimental techniques agreed well with those values obtained by optical methods when expressions derived from the kinetic scheme previously mentioned were employed (see Table I).

The purpose of this paper is to extend the kinetic scheme to results obtained by other workers for changes in intrinsic viscosity as a function of

TABLE I

Value of the Kinetic Parameter $A$ Derived from Infrared Spectroscopy Compared to Those Values of $A$ Obtained from Other Techniques

| Exptl. procedure | Poly-mer | $O_2:N_2$ ratio | Temp. °C | $A$, min$^{-1}$ | |
|---|---|---|---|---|---|
| | | | | From non-optical methods | From infrared spec-troscopy (IR) |
| | Isotactic polypro- | | | | |
| IR (carbonyl)[a] | pylene (IPPr) | 20/80 | 150 | — | 0.021[a] |
| IR (hydroperoxide)[b] | IPPr | 20/80 | 150 | — | 0.021[b] |
| $O_2$-absorption[c] | IPPr | 100/0 | 150 | 0.04[d] | 0.051[d] |
| Oxyluminescence[e,c] | IPPr | 100/0 | 150 | (0.056)$_{av.}$[d] | 0.051[d] |
| From rate of formation of volatile products | | | | | |
| Acetone[f] | IPPr | 53/47 | 130 | 0.010[a] | 0.016[a] |
| Formaldehyde[g] | IPPr | 66/34 | 150 | 0.035[a] | 0.040[a] |
| | Atactic poly- | | | | |
| Intrinsic viscosity[h] | butene-1 | 21/79 | 90 | 0.0037[i] | 0.0044[i] |

[a] Data of Stivala, Reich, et al.[1,3]

[b] Data of Reich and Stivala.[2]

[c] Data of Sehard and Russell.[9]
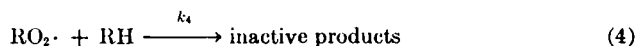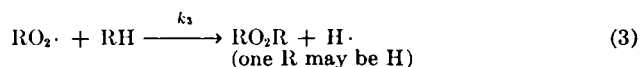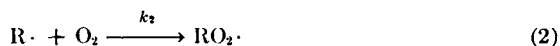
[d] Data of Reich and Stivala.[4]

[e] Data of Ashby.[10]
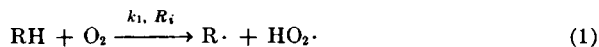
[f] Data of Neiman.[7]

[g] Data of Miller et al.[8]
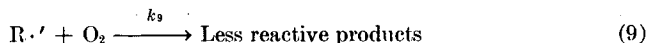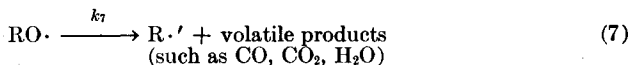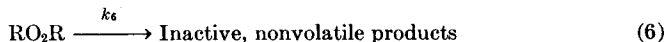
[h] Data of Beati et al.[11]

[i] From this work.

time during the thermal oxidation of atactic polybutene-1.[11] It will be shown that the value of the kinetic parameter, $A$, obtained by the authors for the oxidation of atactic polybutene-1 by optical means[6] agrees well with the value of $A$ obtained from molecular weight versus time data during oxidation of atactic polybutene-1.[11]

## Theory

The mechanism of the uncatalyzed, uninhibited thermal oxidation of polyolefins is given in eqs. (1)–(9). The assumptions employed in deriving kinetic expressions from this scheme have been presented previously.[1,3]

$$RH + O_2 \xrightarrow{k_1, R_i} R\cdot + HO_2\cdot \tag{1}$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \tag{2}$$

$$RO_2\cdot + RH \xrightarrow{k_3} RO_2R + H\cdot \tag{3}$$
(one R may be H)

$$RO_2\cdot + RH \xrightarrow{k_4} \text{inactive products} \tag{4}$$

$$RO_2R \xrightarrow{k_5} 2RO\cdot \tag{5}$$

$$RO_2R \xrightarrow{k_6} \text{Inactive, nonvolatile products} \tag{6}$$

$$RO\cdot \xrightarrow{k_7} R\cdot' + \text{volatile products} \tag{7}$$
$$\text{(such as } CO, CO_2, H_2O)$$

$$R\cdot' + RH \xrightarrow{k_8} R\cdot + R'H \tag{8}$$

$$R\cdot' + O_2 \xrightarrow{k_9} \text{Less reactive products} \tag{9}$$

In this scheme, R represents the polymer backbone and $R_i$ denotes the rate of initiation.

The following expression can be derived from eqs. (1)–(9) for a given temperature and oxygen concentration

$$\rho = K(1 - e^{-At}) \tag{10}$$

where, $\rho$ is the rate of formation of carbonyl groups of nonvolatile products and $K$ and $A$ denote constants. It has been reported by various workers[12] that changes in intrinsic viscosity during polyolefin oxidation is related to carbonyl formation. [Such a relationship would also be anticipated from the scheme; cf. step (6).] From the preceding, we may assume that the number of chain scissions during oxidation ($\Delta n$) is a function of the carbonyl concentration [cf. eq. (11)],

$$\Delta n = f[>C{=}O] = f \int_0^t \rho dt \equiv F_n \tag{11}$$

Also, from eqs. (12) and (13),

$$\Delta n = (M_0/M) - 1 \tag{12}$$

$$[\eta] = K'M^a \tag{13}$$

the following expression can be obtained, if it is assumed that the polymer samples during the oxidation are monodisperse or that they follow a most probable distribution, i.e., $\bar{M}_n/\bar{M}_v = \text{const.}$,

$$\Delta n = ([\eta]_0/[\eta])^{1/a} - 1 \equiv F_n \tag{14}$$

where $M_0$ and $M$ denote number-average molecular weight at the start and during the oxidation, respectively. For heterogeneous systems, during oxidation, Mizutani and co-workers[13] have reported the following expression

$$\Delta n = F_n/f' \tag{14a}$$

where, $f' = [1/(a + 1)!]^{1/a}$. A value of 0.7 was reported for the exponent in eq. (13) for isotactic polybutene-1 in heptane and Decalin[14] which was used in this work.[11]

From eqs. (10), (11), and either (14) or (14a), we may obtain

$$F_n = C/A(At + e^{-At} - 1) \tag{15}$$

where $C$ is a constant. In order to solve eq. (15) for the parameter $A$, we may initially utilize simplified expressions to obtain approximate values of $C$ and $A$. Thus, from eq. (15), we may write for low values of $At$,

$$F_n/t^2 \approx CA/2 - CA^2t/6 \tag{15a}$$

whereas, at high values of $At$, eq. (15) becomes

$$F_n \approx Ct - C/A \tag{15b}$$

In obtaining values of $A$ from eq. (15), we initially utilized the approximate expression (15b).

### Testing of the Theoretical Equations

In Figure 1 we plotted $F_n$ versus time for the air oxidation of atactic polybutene-1 at 90°C. As anticipated, an approximately linear relationship obtained at the higher values of time. From this portion of the curve the following values were obtained: $C = 1.7, A = 0.25$. On substituting these values in eq. (15), the following expression obtains,

$$F_n \approx 7.0\ (0.25t + e^{-0.25t} - 1) \tag{16}$$

Equation (15) may now be written as

$$F_n - 7.0\ e^{-0.25t} \equiv \phi = Ct - C/A \tag{17}$$

An iterative type of procedure was carried out for obtaining values of $A$ by plotting the values of $\phi$ against time. Such plots, shown in Figure 1 exhibit good linearity. Values obtained from the first iteration were: $C = 1.45$ and $A = 0.22$. Now by using these values, another expression similar to eq. (17) was obtained which, from plotting, afforded values of $C = 1.42$ and $A = 0.22$. Since the second iterative process gave values of $C$ and $A$ which were very similar to the preceding values, the value of $A$ was taken as $3.7 \times 10^{-3}$ min$^{-1}$.

In order to compare the above value of $A$, obtained from changes in intrinsic viscosity as a function of time during atactic polybutene-1 oxidation at 90°C, with the corresponding value obtained from rate of formation of carbonyl by means of infrared spectroscopic techniques, it was necessary to extrapolate the values of $A$ obtained between 110 and 130°C to the value at 90°C. Thus, it was necessary to obtain values[6] of $K_2$ and $K_3$ by plotting the logarithms of these values as a function of the reciprocal of the absolute temperature at which they were obtained. Reasonably good linear relations were thereby achieved which gave the following values at 90°C: $K_2 = 4.0$ and $K_3 = 11.8$. From these values at 90°C, the value of $A'(= A/k')$ was obtained which was found to equal 0.88.[6] It was now necessary to estimate $k'$ at 90°C. A good linear plot was obtained
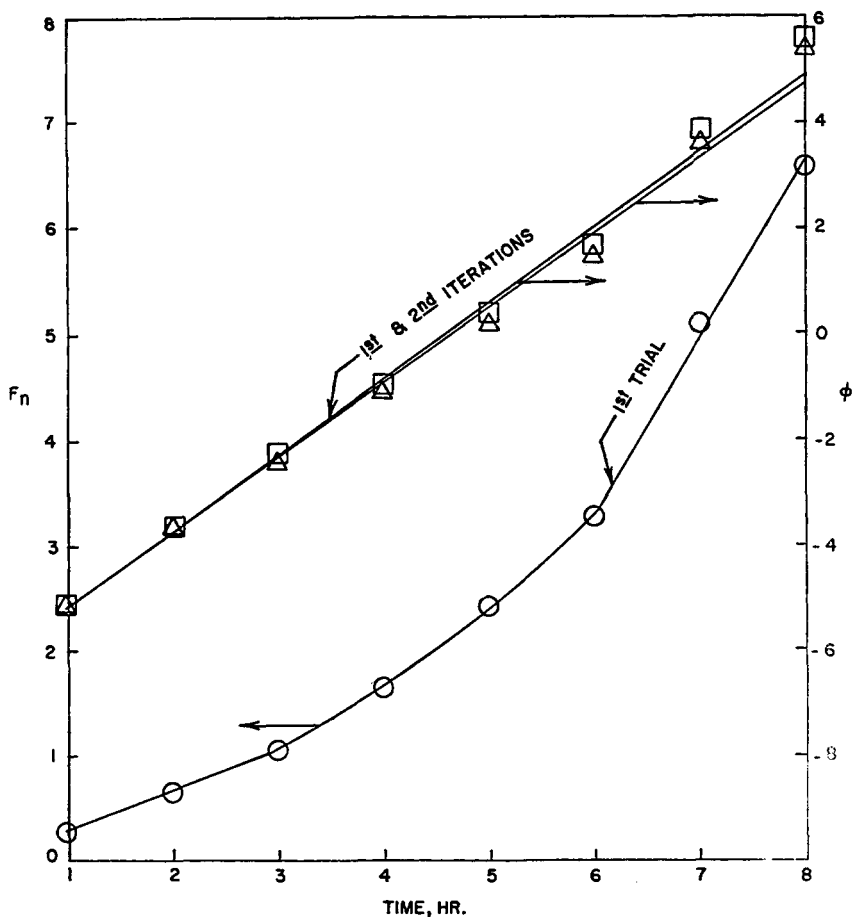
Fig. 1. Plots of $F_n$ and $\phi$ vs. time for the oxidation of atactic polybutene-1 in air at 90°C.

from log $k'$ versus $1/T$, affording a value of $k'$ at 90°C of $5 \times 10^{-3}$. Thus, the extrapolated value of $A$ at 90°C was calculated as $4.4 \times 10^{-3}$ min$^{-1}$, which is in surprisingly good agreement with the value of $A$ obtained from intrinsic viscosity changes, especially when considering that different experimental conditions, different oxidation techniques, and extrapolation procedures were employed. The relatively good agreement obtained for the values of $A$ lends further support to the validity of the scheme employed and to the kinetic expressions derived therefrom.

## References

1. S. S. Stivala, L. Reich, and P. G. Kelleher, *Makromol. Chem.*, **59**, 28 (1963).
2. L. Reich and S. S. Stivala, *J. Polym. Sci. B*, **3**, 227 (1965).
3. S. S. Stivala and L. Reich, *Polym. Eng. Sci.*, **5**, 179 (1965).

4. L. Reich and S. S. Stivala, *J. Polym. Sci. A*, **3**, 4299 (1965).

5. L. Reich and S. S. Stivala, *Revs. Macromol. Chem.*, **1**, 249 (1966).

6. S. S. Stivala, E. B. Kaplan, and L. Reich, *J. Appl. Polym. Sci.*, **9**, 3557 (1965).

7. M. B. Neiman, *Russian Chem. Revs.*, **33**, 13 (1964).

8. V. B. Miller, M. B. Neiman, V. S. Pudov, and L. I. Lafer, *Vysokomol. Soedin.*, **1**, 1696 (1959).

9. M. P. Schard and C. A. Russell, *J. Appl. Polym. Sci.*, **8**, 985 (1964).

10. G. E. Ashby, *J. Polym. Sci.*, **50**, 99 (1961).

11. E. Beati, F. Severini, and G. Clerici, *Makromol. Chem.*, **61**, 104 (1963).

12. H. M. Quackenbos, *Polym. Eng. Sci.*, **6**, 117 (1966).

13. Y. Mizutani, K. Yamamoto, S. Matsuoka and H. Ihara, *Kobunshi Kagaku*, **22**, 97 (1965).

14. S. S. Stivala, R. J. Valles, and D. W. Levi, *J. Appl. Polym. Sci.*, **7**, 97 (1963).