

Autoxidation of Poly(alkylene glycols) in Solution

LEO REICH, *Polymer Research Branch, Picatinny Arsenal, Dover, New Jersey 07801* and S. S. STIVALA, *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

Synopsis

Data reported for the autoxidation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in solution at relatively long reaction times were analyzed. A relatively simple and a more general kinetic scheme with corresponding rate expressions were used. It was found that the more general scheme gave somewhat more satisfactory agreement between calculated and observed values of several reaction variables. Limitations in the applications of both schemes to PEG and PPG autoxidations are mentioned.

INTRODUCTION

A general kinetic scheme for the uncatalyzed, uninhibited autoxidation of polypropylene in the bulk phase was first reported by Stivala et al. in 1963.¹ Since then, they have reported on various kinetic aspects of the autoxidation of polyolefins in the bulk phase using this general scheme. Thus, rates of carbonyl and hydroperoxide formation,²⁻⁵ oxygen absorption,^{6,7} and volatile products^{3,5} formation were investigated along with chemiluminescence,^{5,6} changes in intrinsic viscosity as a function of time,^{8,9} and autoxidation in the presence of inhibitors.¹⁰ Recently, Bawn and Chaudhri^{11,12} successfully extended the general scheme presented by Reich, Stivala, and co-workers to the autoxidation of polypropylene in solution (at relatively high polymer concentrations). At relatively low polymer concentrations, a much simpler scheme was found to be valid in which termination of polymeric peroxy radicals by recombination was postulated¹³ (which the general scheme mentioned earlier did not include).

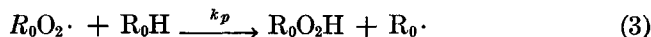
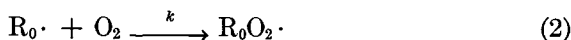
Recently, Grosborne and co-workers¹⁴ reported on a kinetic study of the autoxidation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in solution in the presence of the free-radical initiator azodicyclohexanenitrile (ADCN). These investigators developed kinetic expressions which could satisfactorily explain various aspects of the autoxidation of PEG and PPG during initial reaction conditions (at very low conversions). They assumed that termination of polymeric peroxy radicals by recombination occurred along with intra- and intermolecular propagation. However, these workers did not analyze their data for the autoxidation of PEG and PPG as a function of reaction time (for relatively high conversions).

It is the purpose of this paper to present an analysis of the data obtained by Grosborne and co-workers¹⁴ for the autoxidation of PEG and PPG as a function of reaction time. We will utilize basic ideas previously presented in our general scheme¹⁻¹⁰ for the formation of carbonyl moieties and of hydroperoxide, and for changes in intrinsic viscosity as a function of reaction time. Two schemes will be employed in our analysis. Both will involve free radical processes; however, a major difference is that one involves termination of polymeric peroxy radicals by recombination (simple scheme) whereas the other does not (general scheme).

THEORY

Scheme with Termination of Polymeric Peroxy Radicals by Recombination

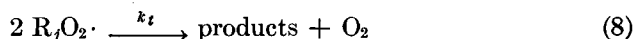
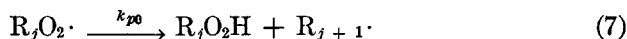
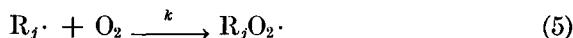
During the initial stages for the autoxidation of PEG and PPG in solution, the scheme shown in eqs. (1)–(8) was assumed to apply.¹⁴



.

.

.

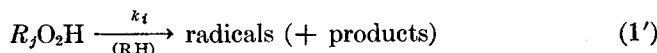


Here, k_{p0} and k_p denote the rate constants for intra- and intermolecular propagation, respectively; and, R_0H represents the unoxidized substrate. For relatively long kinetic chain lengths and from steps (1)–(8), the following rate of oxidation (ρ_{0x}) expression may be obtained:¹⁴

$$\rho_{0x} = R_p + (R_t + R_p) \sum_{j=1}^n \left(\frac{k_{p0}}{D} \right)^j \quad (9)$$

where $R_p = k_p[\text{R}_0\text{H}]R_t^{1/2}k_t^{-1/2}$, R_t denotes the rate of radical initiation from ADCN; $D = k_{p0} + k_p[\text{R}_0\text{H}] + (k_t R_t)^{1/2}$; and, n denotes the number of successive intramolecular propagations.

At relatively high conversions, eq. (9) should no longer be valid, and the following additional initiation step must be considered,



Thus, at long reaction times, it would be anticipated that the concentration of hydroperoxide would attain a relatively high limiting value.^{15,16} Since the rate constant for polypropylene hydroperoxide decomposition^{7,17} is about thirty times that for ADCN decomposition at 95°C, it would be expected that as the autoxidation proceeds and the PEG and PPG hydroperoxide concentration rises, initiation via hydroperoxide decomposition (R_i') would predominate over initiation via ADCN decomposition (R_i).

Rate of Hydroperoxide Formation. From the preceding, we may write for the initiation rate after initial oxidation stages,

$$R_i' = 2 k_i \sum [R_j O_2 H] \quad (10)$$

Furthermore, it is assumed that intramolecular propagation is inoperative during the autoxidation at relatively high reaction times. Due to chain scission during the autoxidation, the number of hydrogens per polymer molecule which would be available for intramolecular propagation would be greatly diminished (also, the inclusion of intramolecular propagation resulted in kinetic expressions which gave calculated values of variables which disagreed more with observed values than when intramolecular propagation was neglected). Thus, we may also write,

$$d(\Sigma [R_j O_2 H])/dt \equiv \rho_{HP} = k_p [RH] \Sigma [R_j O_2 \cdot] - (R_i'/2) \quad (11)$$

$$\rho_{HP} = \{k_p [RH] (k_i \Sigma [R_j O_2 H])^{1/2} / k_i^{1/2}\} - k_i \Sigma [R_j O_2 H] \quad (12)$$

Assuming that k_p , k_i , and $[RH]$ are approximately constant during the PEG autoxidation, eq. (12) may be integrated to give

$$\ln \{1 - (k_i/B) [HP]^{1/2}\} = - (k_i/2)t \quad (13)$$

where

$$B = k_i^{1/2} k_i^{-1/2} k_p [RH]$$

$$[HP] = \Sigma [R_j O_2 H]$$

At relatively long reaction times, $B/K_i = [HP]_{\infty}^{1/2}$, and eq. (13) becomes

$$\ln \{1 - ([HP]/[HP]_{\infty})^{1/2}\} = - (k_i/2)t \quad (14)$$

Upon differentiating, eq. (14) becomes,

$$\ln(\rho_{HP}/[HP]^{1/2}) = \ln B - (k_i/2)t \quad (15)$$

Expressions will now be derived from the preceding equations for rates of autoxidation ρ_{oz} and ester formation ρ_{CO} , and for changes in intrinsic viscosity as a function of reaction time.

Rate of Autoxidation. The rate of oxidation is given by

$$\rho_{oz} = k [O_2] \Sigma [R_j \cdot] - R_i/2 \quad (16)$$

and

$$\rho_{CO} = k_i [HP] + \{k_p [RH] (k_i [HP])^{1/2} / k_i^{1/2}\} \quad (17)$$

Upon substituting the expression for [HP] from eq. (14) into eq. (17) and integrating,

$$\Delta[\text{O}_2] = 2 k_t[\text{HP}]_\infty t + 6[\text{HP}]_\infty (e^{-(k_t/2)t} - 1) - [\text{HP}]_\infty (e^{-k_t t} - 1) \quad (18)$$

Rate of Ester Formation. From previously reported work,²⁻⁵

$$\rho_{\text{CO}} = f k_t [\text{HP}] \quad (19)$$

where f denotes a proportionality factor. Upon combining eqs. (14) and (19), the following expressions can be derived,

$$\Delta\left(\left[\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}=\text{O} \right] \right) = (\rho_{\text{CO}})_\infty t + 4 \frac{(\rho_{\text{CO}})_\infty}{k_t} (e^{-(k_t/2)t} - 1) - \frac{(\rho_{\text{CO}})_\infty}{k_t} (e^{-k_t t} - 1) \quad (20)$$

and

$$\ln\{1 - [\rho_{\text{CO}}/(\rho_{\text{CO}})_\infty]^{1/2}\} = - (k_t/2)t \quad (20')$$

where

$$(\rho_{\text{CO}})_\infty = f k_t [\text{HP}]_\infty$$

Intrinsic Viscosity Changes. Based upon previously reported work,^{8,9} let

$$\Delta\eta \equiv ([\eta]_0/[\eta])^{1/\alpha} - 1 = f_1 \left[\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}=\text{O} \right] \quad (21)$$

where, f_1 is a proportionality factor; $[\eta]_0$ and $[\eta]$ denote intrinsic viscosities which PEG possesses initially and during autoxidation, respectively; and, α is the Mark-Houwink exponent (0.77 for PEG). Substituting the expression for $[\text{>C=O}]$ from eq. (20) into eq. (21) yields

$$\Delta\eta = f_1 (\rho_{\text{CO}})_\infty t + 4 f_1 \frac{(\rho_{\text{CO}})_\infty}{k_t} (e^{-(k_t/2)t} - 1) - \frac{f_1 (\rho_{\text{CO}})_\infty}{k_t} (e^{-k_t t} - 1) \quad (22)$$

Scheme without Termination of Polymeric Peroxy Radicals by Recombination

The general scheme and the corresponding equations derived therefrom¹⁻¹⁰ were utilized to obtain expressions for various variables in the autoxidation of PEG and PPG.

Rate of Hydroperoxide Formation. From the general scheme previously referred to, it can readily be shown that,

$$[\text{HP}] \cong [\text{HP}]_\infty (1 - e^{-A t}) \quad (23)$$

or

$$\ln\{1 - ([\text{HP}]/[\text{HP}]_\infty)\} = - A t \quad (23a)$$

Upon differentiating, eq. (23) becomes

$$\rho_{\text{HP}} = A [\text{HP}]_{\infty} e^{-At} \quad (24)$$

or

$$\ln \rho_{\text{HP}} = \ln(A [\text{HP}]_{\infty}) - At \quad (24a)$$

Rate of Ester Formation. It can be shown¹⁻¹⁰ that

$$\rho_{\text{CO}} = (\rho_{\text{CO}})_{\infty}' (1 - e^{-At}) \quad (25)$$

where $(\rho_{\text{CO}})_{\infty}' = k_6 [\text{HP}]_{\infty}$. Equation (25) may be rearranged to give

$$\ln[1 - \rho_{\text{CO}}/(\rho_{\text{CO}})_{\infty}'] = -At \quad (25a)$$

Furthermore, from eq. (25),

$$\Delta \left(\left[\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}=\text{O} \right] \right) = (\rho_{\text{CO}})_{\infty}' t + \frac{(\rho_{\text{CO}})_{\infty}'}{A} (e^{-At} - 1) \quad (26)$$

Rate of Autoxidation. The rate of autoxidation is given by

$$\rho_{\text{OX}} = R_t + k_5 [\text{HP}] \quad (27)$$

and

$$\rho_{\text{OX}} = R_t + k_5 [\text{HP}]_{\infty} (1 - e^{-At}) \quad (28)$$

From eq. (28),

$$\Delta[\text{O}_2] = R_t t + k_5 [\text{HP}]_{\infty} t + (k_5 [\text{HP}]_{\infty} / A) (e^{-At} - 1) \quad (29)$$

Intrinsic Viscosity Changes. Substituting eq. (26) into eq. (21) yields

$$\Delta\eta = f_1 (\rho_{\text{CO}})_{\infty}' t + [f_1 (\rho_{\text{CO}})_{\infty}' / A] (e^{-At} - 1) \quad (30)$$

In the next section, eqs. (14), (15), (18), (20), (22)–(24), (26), and (29) will be applied to data for the autoxidation of PEG ($\bar{M}_n = 25,000$) and PPG ($\bar{M}_n = 10^6$) in *o*-dichlorobenzene at 94 and 85°C, respectively. The results will be tabulated and compared.

RESULTS

In Figures 1 and 2 are shown plots of eqs. (14) and (15). Values of $[\text{HP}]_{\infty}^{1/2} = 0.45$ and 0.20 were used for PEG and PPG, respectively. From the linear relationships obtained, average values of k_t of $4.4 \times 10^{-4} \text{ sec}^{-1}$ and $7.5 \times 10^{-4} \text{ sec}^{-1}$ were obtained from eqs. (14) and (15) for PEG and PPG, respectively. A good linear plot would be anticipated at the higher reaction times ($R_t' \gg R_t$); cf. plot of eq. (14) of Figures 1 and 2. Using the following values¹⁴ for PEG at the higher reaction times: $[\text{RH}] = 4.2$, $k_p = 3$, and $k_t = 10^6$, the intercept from the plot of eq. (15) affords a value from which a value of $k_t = 1 \times 10^{-4} \text{ sec}^{-1}$ can be calculated. Thus, there appears to be a large discrepancy between the value of k_t obtained from the slopes of the plots of eqs. (14) and (15) and the value obtained

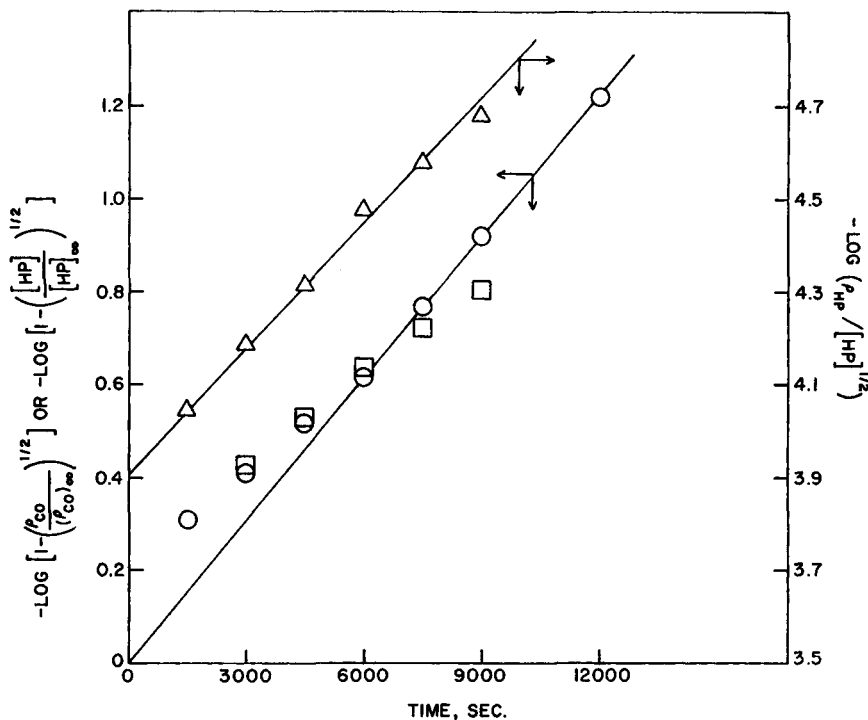


Fig. 1. Plots of eqs. (14), (15), and (20') for the autoxidation of PEG: (○) eq. (14); (Δ) eq. (15); (□) eq. (20').

from the intercept of the plot of eq. (15). This inconsistency may be partially due to the values assumed for $[RH]$, k_p , and k_t and/or to the assumptions made in deriving eqs. (14) and (15). A similar inconsistency was observed for PPG.

In Figures 3 and 4 are shown plots of eqs. (23a), (24a), and (25a). From plots of these respective equations, average values of A of $1.40 \times 10^{-4} \text{ sec}^{-1}$ and $2.62 \times 10^{-4} \text{ sec}^{-1}$ were obtained for PEG and PPG, respectively. From the value of the intercepts obtained from the plots of eq. (24a) and the values of A obtained from their slopes, values of $[HP]_{\infty} = 0.20$ and 0.041 were calculated for PEG and PPG, respectively (observed, 0.20 and 0.040). Thus, values obtained from the slopes and intercepts of plots are in better agreement with the more general scheme than the simpler scheme.

From known values of k_t and $[HP]_{\infty}$, eq. (18) may be written for PEG and PPG, respectively, as

$$\Delta[O_2] = 1.76 \times 10^{-4}t + 1.20(e^{-2.2 \times 10^{-4}t} - 1) - 0.20(e^{-4.4 \times 10^{-4}t} - 1) \quad (18a)$$

$$\Delta[O_2] = 0.60 \times 10^{-4}t + 0.24(e^{-3.75 \times 10^{-4}t} - 1) - 0.040(e^{-7.5 \times 10^{-4}t} - 1) \quad (18b)$$

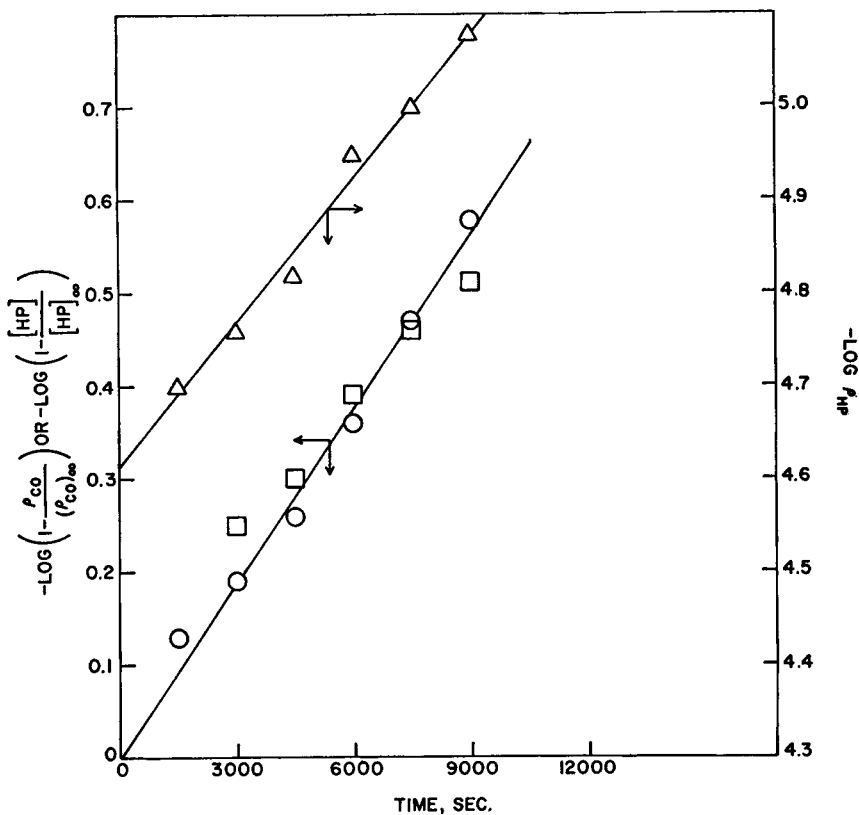


Fig. 2. Plots of eqs. (14), (15), and (20') for the autoxidation of PPG: (O) eq. (14); (Δ) eq. (15); (□) eq. (20').

TABLE I
Calculated and Observed Values of $\Delta[\text{O}_2]$ for PEG and PPG

	Time $\times 10^{-4}$, sec	$\Delta[\text{O}_2]$, mole/l.		
		Calculated ^a		Observed
		Eq. (18)	Eq. (29)	
PEG	0.30	0.10	0.07	0.11
	0.45	0.16	0.13	0.16
	0.60	0.35	(0.20)	0.20
	0.75	0.54	0.29	0.25
	0.90	0.75	0.39	0.29
PPG	0.15	0.014	0.0085	0.015
	0.30	0.055	(0.028)	0.028
	0.45	0.11	0.056	0.040
	0.60	0.18	0.090	0.050

^a For PEG, calculations of $\Delta[\text{O}_2]$ are based on eqs. (18a) and (29a); for PPG calculations are based on eqs. (18b) and (29b).

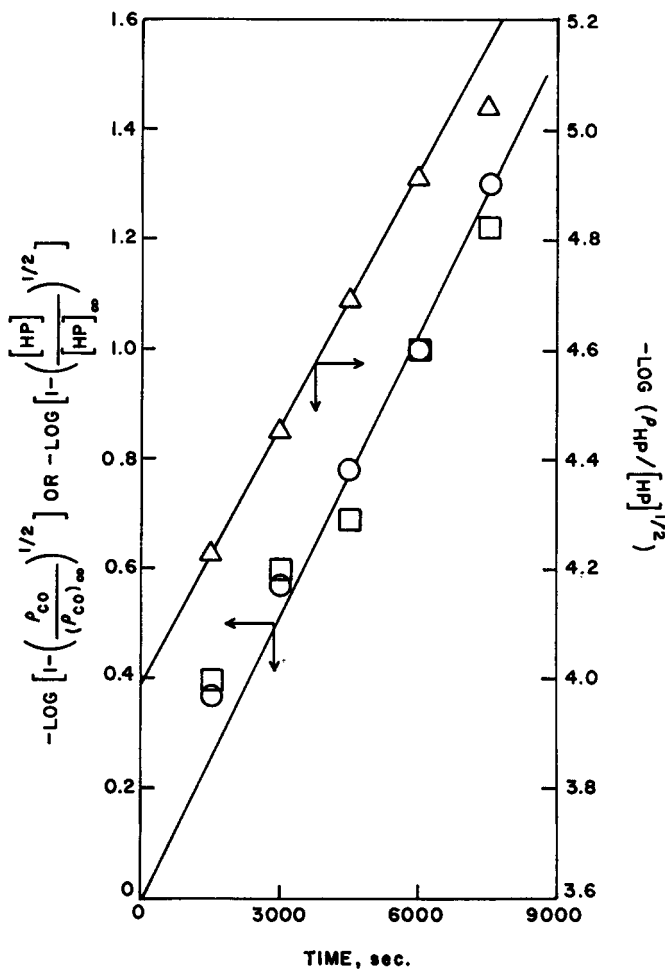


Fig. 3. Plots of eqs. (23a), (24a), and (25a) for the autoxidation of PEG: (O) eq. (23a); (Δ) eq. (24a); (\square) eq. (25a).

Table I contains calculated [eqs. (18a), (18b), (29a), (29b)] and observed values of $\Delta[\text{O}_2]$ at various reaction times for PEG and PPG.

Prior to using eq. (20) to estimate values of $\Delta[>\text{C}=\text{O}]$ for PEG, its first corresponding expressions were obtained from eq. (29) (from the general scheme) by utilizing known values of R_i , A , $[\text{HP}]_\infty$, and a particular value of $\Delta[\text{O}_2]$ at a certain reaction time, e.g., $\Delta[\text{O}_2] = 0.20$ at $t = 0.6 \times 10^4$ sec for PEG and $\Delta[\text{O}_2] = 0.028$ at $t = 0.3 \times 10^4$ sec for PPG. From these values of $k_5 = 4.8 \times 10^{-4} \text{ sec}^{-1}$ and $7.1 \times 10^{-4} \text{ sec}^{-1}$ were estimated for PEG and PPG, respectively [cf. the corresponding values of $k_4 \cong 4.4 \times 10^{-4} \text{ sec}^{-1}$ and $7.5 \times 10^{-4} \text{ sec}^{-1}$ obtained from eqs. (14) and (15) for PEG and PPG, respectively]. Equation (29) may now be written for PEG and PPG,

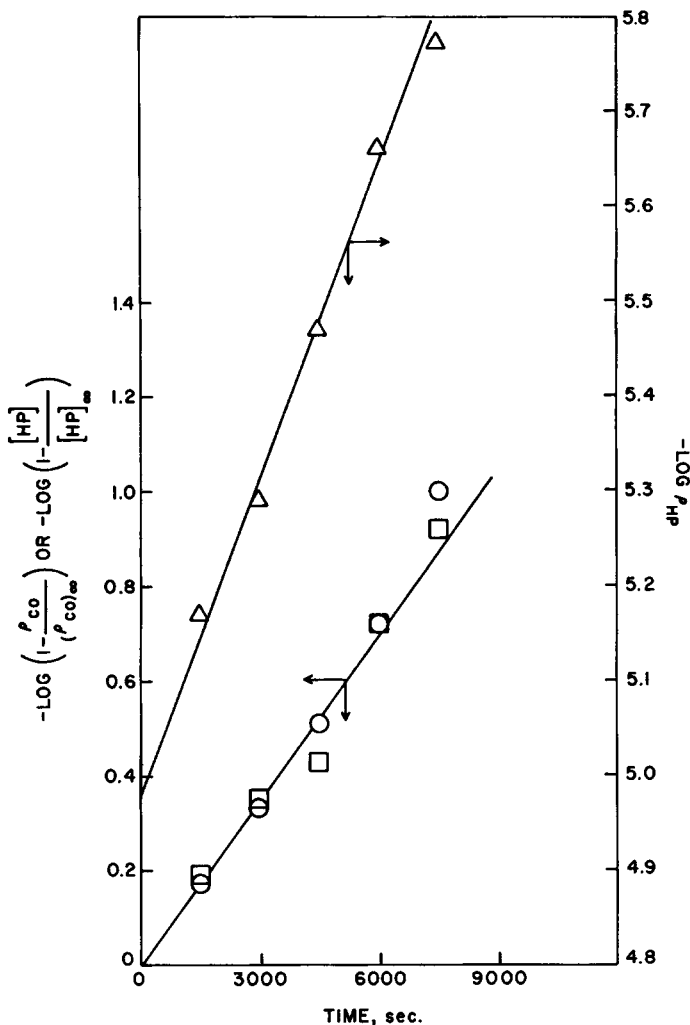


Fig. 4. Plots of eqs. (23a), (24a), and (25a) for the autoxidation of PPG: (O) eq. (23a); (Δ) eq. (24a); (\square) eq. (25a).

respectively, as

$$\Delta[\text{O}_2] = 0.98 \times 10^{-4}t + 0.69 (e^{-1.4 \times 10^{-4}t} - 1) \quad (29a)$$

and,

$$\Delta[\text{O}_2] = 0.29 \times 10^{-4}t + 0.11 (e^{-2.6 \times 10^{-4}t} - 1) \quad (29b)$$

necessary to obtain the value of $(\rho_{CO})_{\infty}$. By employing a value of $(\rho_{CO})_{\infty} = 0.22 \times 10^{-4}$, a plot of Eq. (20') afforded an approximate linear relationship which overlapped the plot for Eq. (14), as would be anticipated, cf. Fig. 1. Similar considerations apply when $(\rho_{CO})_{\infty} = 0.60 \times 10^{-5}$ was used for PPG, cf. Fig. 3. Equation (20) now becomes for PEG and PPG, respectively,

$$\Delta[>C=O] = 0.22 \times 10^{-4}t + 0.20(e^{-2.2 \times 10^{-4}t} - 1) - 0.05(e^{-4.4 \times 10^{-4}t} - 1) \quad (20a)$$

and,

$$\Delta[>C=O] = 0.60 \times 10^{-5}t + 0.032(e^{-3.75 \times 10^{-4}t} - 1) - 0.008(e^{-7.5 \times 10^{-4}t} - 1) \quad (20b)$$

The corresponding expressions for $\Delta[>C=O]$ from the general scheme may be similarly obtained as follows: if we utilize a value of $(\rho_{CO})_{\infty}' = 0.22 \times 10^{-4}$ in eq. (25a), a plot of this equation (cf. Fig. 3) also gives a plot which overlaps that from eq. (23a), as would be expected. From this value of $(\rho_{CO})_{\infty}'$, eq. (26) becomes for PEG,

$$\Delta[>C=O] = 0.22 \times 10^{-4}t + 0.155(e^{-1.4 \times 10^{-4}t} - 1) \quad (26a)$$

Similarly, when a value of $(\rho_{CO})_{\infty}' = 0.60 \times 10^{-5}$ is used in eq. (25a), a plot of this equation (cf. Fig. 4) also gives a plot which overlaps that from eq. (23a). Equation (26) becomes for PPG,

$$\Delta[>C=O] = 0.60 \times 10^{-5}t + 0.023(e^{-2.62 \times 10^{-4}t} - 1) \quad (26b)$$

Table II summarizes calculated [from eqs. (20a), (20b), (26a), and (26b)] and observed values of $\Delta[>C=O]$ at various reaction times for PEG and PPG, respectively.

TABLE II
Calculated and Observed Values of $\Delta[>C=O]$ for PEG and PPG

	Time $\times 10^{-4}$, sec.	$\Delta[>C = O]$, mole/l.		
		Calculated*		Observed
		Eq. (20)	Eq. (26)	
PEG	0.30	0.01	0.014	0.019
	0.60	0.032	0.044	0.055
	0.90	0.074	0.088	0.10
	1.2	0.13	0.14	0.15
PPG	0.15	0.0007	0.0014	0.002
	0.30	0.004	0.0054	0.0077
	0.60	0.016	0.018	0.020
	0.90	0.034	0.033	0.034

* For PEG calculations of $\Delta[>C = O]$ are based on eqs. (20a) and (26a); for PPG calculations are based on eqs. (20b) and (26b).

Prior to using eq. (22) to estimate values of $\Delta\eta$, a value of f_1 must be obtained. From data provided,¹⁴ a value of $f_1 = 60$ was estimated for PEG. Then eq. (22) becomes for PEG:

$$\Delta\eta = 13.2 \times 10^{-4}t + 12(e^{-2.2 \times 10^{-4}t} - 1) - 3(e^{-4.4 \times 10^{-4}t} - 1) \quad (22a)$$

Sufficient data were not available for a similar treatment for PPG.

The corresponding expression for $\Delta\eta$ from the general scheme, Eq. (30), becomes for PEG,

$$\Delta\eta = 13.2 \times 10^{-4}t + 9.3 (e^{-1.4 \times 10^{-4}t} - 1) \quad (30a)$$

In Table III are listed calculated [from eqs. (22a) and (30a)] and observed values of $[\eta]$ at various reaction times.

TABLE III
Calculated and Observed Values of $[\eta]$ for PEG

Time $\times 10^{-4}$ sec	$[\eta]$, dl/g		
	Calculated		Observed
	Eq. (22a)	Eq. (30a)	
0.30	0.46	0.35	0.27
0.45	0.33	0.26	0.22
0.60	0.24	0.21	0.19
0.75	0.18	0.17	0.17
0.90	0.15	0.14	0.15

DISCUSSION

It is noted from Tables I-III that use of the simple kinetic scheme yields expressions which afford values of various parameters that are in poorer agreement to those obtained from the expressions derived from the more general scheme.¹⁻¹⁰ Further, although both eqs. (15) and (24a) (from the simple and more general scheme, respectively) afford linear plots (cf. Figs. 1 and 3), values derived from the slope and intercept of the plotted eq. (15) are inconsistent whereas they are consistent for the plot of eq. (24a). Interestingly, both schemes yield values of rate constants at 95°C for PEG hydroperoxide decomposition ($k_t = 4.4 \times 10^{-4} \text{ sec}^{-1}$ and $k_s = 4.8 \times 10^{-4} \text{ sec}^{-1}$) which are in good agreement. Chien and Boss¹⁷ have indicated a value of about $1 \times 10^{-4} \text{ sec}^{-1}$ for the rate constant for polypropylene hydroperoxide decomposition at 95°C. The values of $(\rho_{CO})_\infty$ are similar for both schemes. At relatively large reaction times, there are large discrepancies between values obtained for $\Delta[O_2]$ from both schemes. This behavior may be due to the formation of oxidation products at the high reaction times which inhibit the oxidation rate. This is postulated in view of the fact that the oxidation rates of polyolefins¹⁷ generally increase more rapidly than observed for PEG.

It may also be mentioned that when intramolecular propagation was included in the simple scheme, greater discrepancies between calculated and observed values of reaction variables resulted than when it was neglected. As previously indicated, after initial reaction times, chain scission occurs to a great extent, thereby lessening the number of hydrogens per polymer molecule available for intramolecular propagation.

Despite the somewhat better agreement provided by the more general

scheme between calculated and observed reaction variables, it is difficult to account for the change in mechanism that apparently results after initial autoxidation (very low conversion) times, i.e., termination by recombination of polymeric peroxy radicals no longer occurs after initial reaction times. In view of this and discrepancies between calculated and observed values at relatively low and high reaction times, (at relatively low reaction times, discrepancies would be expected for the simple scheme) more work on PEG autoxidation is indicated before any final decision can be reached as to which scheme is preferable.

This work was supported, in part, by a grant from the Office of Naval Research to Stevens Institute of Technology.

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, *Polymer Eng. Sci.*, **5**, 179 (1965).
4. S. S. Stivala, E. B. Kaplan, and L. Reich, *J. Appl. Polym. Sci.*, **9**, 3557 (1965).
5. L. Reich and S. S. Stivala, *Revs. Macromol. Chem.*, **1**, 249 (1966).
6. L. Reich and S. S. Stivala, *J. Polym. Sci. A*, **3**, 4299 (1965).
7. L. Reich and S. S. Stivala, *J. Appl. Polym. Sci.*, **12**, 2033 (1968).
8. L. Reich and S. S. Stivala, *J. Appl. Polym. Sci.*, in press.
9. L. Reich and S. S. Stivala, *J. Appl. Polymer Sci.*, in press.
10. S. S. Stivala and L. Reich, *Polymer Eng. Sci.*, **7**, 253 (1967).
11. C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 81 (1968).
12. C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 123 (1968).
13. C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 113 (1968).
14. P. Grosborne, I. S. deRoch, and L. Sajus, *Bull. Chim. Soc., France*, **1968**, 2020.
15. A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **72**, 1942 (1950).
16. L. Dulog and G. Storck, *Makromol. Chem.*, **91**, 50 (1966).
17. J. C. W. Chien and C. R. Boss, *J. Polym. Sci. A-1*, **5**, 3091 (1967).

Received October 8, 1968