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Effect of Oxygen on the Polymerization of Vinyl Chloride

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ABSTRACT

The effects of oxygen on the liquid-phase polymerization of vinyl chloride at 55°C in the presence of an added initiator, bis(4-tert-butylcyclohexyl) peroxydicarbonate, (Perkadox 16), have been studied by tumbled dilatometry. A conventional kinetic scheme involving a predominant cross-termination reaction is proposed to explain the dependence of the induction period on initial oxygen concentration and initiator concentration. The degree of conversion of the initial oxygen to peroxidic compounds did not exceed 30% by weight under any experimental conditions employed, and the existence of other oxidation products such as formaldehyde, carbon monoxide, and methanol has been demonstrated. Radical decomposition reactions may produce some of the oxidation products. At 55°C, the average velocity constant for decomposition of vinyl chloride polyperoxides in dichloromethane solution was $8 \times 10^{-5} \text{ sec}^{-1}$ compared with $6.6 \times 10^{-5} \text{ sec}^{-1}$ for Perkadox 16. Perkadox 16 has been used as an initiator in a dilatometric study of the homogeneous

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polymerization of styrene at 60°C. Molecular weights of the polymers were determined viscometrically or by the use of gel-permeation chromatography. The results indicate that no transfer to initiator occurs in this system.

INTRODUCTION

The free-radical autoxidation of many saturated organic compounds, R'H, in the liquid phase at moderate temperatures (<100°C) and relatively high pressures (>100 torr) has been extensively studied and reviewed [1, 2]. Under such conditions, the rate-determining propagation step involves attack of a peroxy radical R'O₂· on R'H to produce a hydroperoxide R'OOH and an alkyl radical R'·.

Termination involves two peroxy radicals, and consequently the overall rate of oxidation is independent of oxygen pressure.

At relatively high oxygen concentrations, the autoxidation of many vinyl monomers, CH₂=CXY, proceeds similarly, except that propagation involves addition to the double bond and polyperoxides, $\left(\text{CH}_2\text{-CXY-O-O}\right)_n$, are usually assumed to be the main reaction

products. Thus this mechanism is applicable to styrene in bulk [3] and emulsion [4], acrylonitrile [5], methyl methacrylate [6], vinyl acetate [7], and other monomers [8, 9].

The effect of oxygen at lower pressures on vinyl polymerizations has been studied less frequently. Termination may then occur predominantly by a cross-combination of peroxy-type radicals RO₂· with other radicals R·, so the oxidation rate becomes dependent on the square root of the oxygen concentration. Cross termination has been claimed for styrene [10], α -methylstyrene [11], and methyl methacrylate [12]. Under these conditions, when scavenging of radicals by oxygen is less efficient, radical decomposition may occur to give by-products, including epoxides.

Previous workers have noted, qualitatively, that the addition of oxygen to vinyl chloride radical polymerizations produced an induction period [13-16], before precipitation of homopolymer PVC. Quantitatively, Mørk [17] has shown that for an emulsion system at 50°C, the induction period τ was proportional to the square root of the initial oxygen concentration, and a similar dependence has been noted recently [18] for the bulk system at 55°C. In marked contrast, Machacek and Cermak [19], studying vinyl chloride at 35°C in the presence of 10-300 ppm w/w of oxygen, found that the rate of oxygen consumption was independent of oxygen concentration. A very low

rate of initiation was employed, however, and this, together with appreciable experimental errors, makes comparison with the results of other workers, difficult. Both Machacek and Cermak [19] and Mørk [17] report a half-order dependence of the rate of oxygen uptake on the initiator concentration and consistent with this result, Garton and George [18] found that their induction periods varied inversely as the square root of the initiator concentration at constant oxygen concentration.

This paper summarizes previous work, includes the results of more recent studies, and assesses the relative susceptibility of vinyl chloride towards oxidation. The kinetic characteristics of Perkadox 16, used as an initiator, is also reported for the polymerization of the model monomer, styrene, at 60°C.

EXPERIMENTAL

Materials

Vinyl chloride (BP Chemicals Int. Ltd., pilot plant grade) was purified by partial polymerization in vacuo at 0°C by use of 2,2'-azobisisobutyronitrile (AIBN), exposed to ultraviolet light, as initiator. After degassing on the vacuum line, the monomer was distilled from the insoluble polymer and stored as a gas in darkened 10 dm³ bulbs. This purification technique has previously been shown to be satisfactory [18]. Styrene was purified as described previously [20].

Bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16, Novadel Ltd.) was recrystallized twice from AR ethanol, dried in vacuo at room temperature, and stored at -20°C until required. Iodometric titration [21] indicated > 99% purity.

2,2'-Azobisisobutyronitrile (AIBN, Ralph N. Emmanuel Ltd.) was recrystallized twice from AR methanol, dried in vacuo at room temperature, and stored at -20°C until required; mp 101.8-102.4°C with decomposition.

A medical grade oxygen (British Oxygen Co. Ltd.,) was used and stored in a 10 dm³ bulb on the vacuum line.

Dilatometry

Conventional dilatometry was carried out in Pyrex vessels of 15 mm o.d., 1.75 mm wall thickness, having bulb volumes of about 2.5 cm³ and with 2 mm precision bore capillary. These dilatometers

were filled with initiator, vinyl chloride, and oxygen in the usual way [18] and then placed, clamped vertically, in a thermostat at $55 \pm 0.02^\circ\text{C}$. The end of the induction period was indicated by a sudden rapid decrease in the meniscus height.

The above technique produced inconsistent results, and in another method, the dilatometer bulbs were of a larger size. The dilatometers were each tumbled at about 30 rpm with the gas phase initially within the bulb.

In this "tumbled dilatometry," the end of the induction period was noted by the onset of polymer precipitation. Rates of polymerization were subsequently measured with these dilatometers clamped vertically [18].

Although Perkadox 16 was commonly used as initiator in the studies involving vinyl chloride, there appears to be no quantitative data, reported in the literature, concerning its kinetic behavior. For this reason its behavior was examined in separate conventional dilatometric experiments at 60°C by use of styrene as a model monomer. Homogeneous polymerizations were carried out in bulk and in toluene solution at 60°C , and molecular weights of the isolated polystyrenes were determined by gel-permeation chromatography (GPC) or by a viscometric technique with toluene as a solvent at 30°C .

Conversion of Oxygen to Peroxidic Products

AIBN, rather than Perkadox 16, was used in a series of experiments with vinyl chloride and added oxygen in order to avoid interference in peroxide determinations. With a known initial amount of oxygen, the total peroxide content at the end of the induction period was determined using the mild acetic acid-potassium iodide method of Banerjee and Budke [22], with the liberated iodine estimated spectrophotometrically. The more vigorous method of Mair and Graupner [23] produced closely similar results.

The effect of the gas-phase volume on the conversion of initial oxygen to peroxide was examined by using vessels with different gas-phase volumes, and the effect of tumbling was also assessed.

The rate of decomposition of the peroxide products, prepared with the use of AIBN, was determined in dichloromethane solution at 55°C , and a sample of Perkadox 16 was also examined in the same solvent [18].

Oxidation Product Identification

Apart from the determination of the percent conversion of initial oxygen to peroxides, attempts were made to identify the volatile

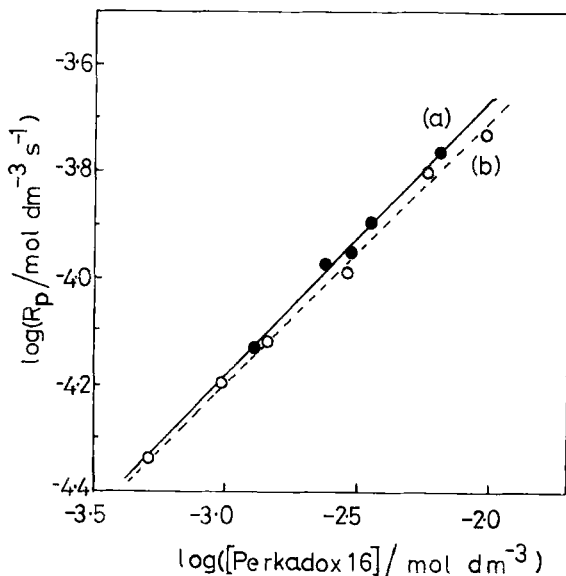


FIG. 1. Logarithmic plot of the rate of polymerization R_p , of bulk styrene at 60°C as a function of the logarithm of mean Perkadox 16 concentration, $\log [\text{Perkadox 16}]$: (a), (b) are results for two separate sets of experiments using a different supply of styrene.

oxidation products. Samples isolated at the end of the induction periods were fractionated at low temperature and different fractions were examined by a variety of techniques including gas chromatography, (Pye-Unicam 104), infrared spectrometry (Perkin-Elmer 137G), and microwave plasma detection, (MPD 850, Applied Research Laboratories Ltd., Luton).

RESULTS AND DISCUSSION

Kinetic Characteristics of Perkadox 16 and Polyperoxides of Vinyl Chloride

In the dilatometric experiments at 60°C with Perkadox 16 and with styrene as a model monomer [24], a linear relationship was obtained

in the plot of the logarithm of rate of polymerization against the logarithm of initiator concentration (Fig. 1).

In one set of experiments, (Fig. 1a) the log-log plot indicated that the rate of bulk styrene polymerization R_p depended on the mean Perkadox 16 concentration to the 0.52 power, while in another set of experiments (Fig. 1b), the initiator exponent was 0.48. The mean initiator exponent was thus 0.50, and in toluene solution polymerizations, R_p was found to be directly proportional to the mean monomer concentration, in accordance with simple theory.

A plot of reciprocal degrees of polymerization ($1/\overline{DP}$) against rates R_p for the bulk polymerization of styrene at 60°C is shown in Fig. 2. Although there was some discrepancy between values of \overline{DP} calculated from GPC and viscometric results, there appears from Fig. 2 to be no evidence of polymer radical transfer to Perkadox 16 [25].

Analysis of the data shown in Fig. 1 enabled a value of $2k_1f$ to be found for Perkadox 16 at 60°C in styrene, where k_1 is the first-order

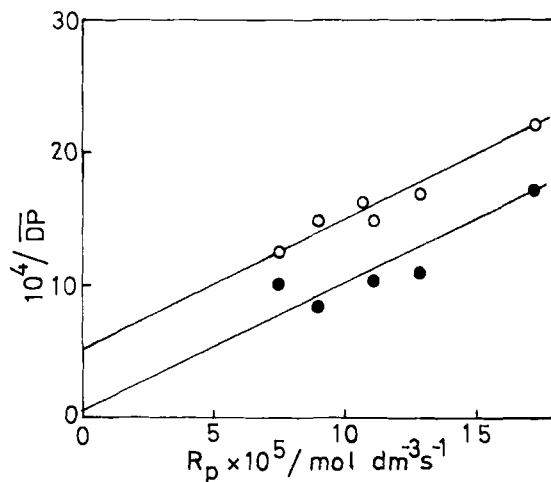


FIG. 2. Reciprocal degrees of polymerization $1/\overline{DP}$ as a function of polymerization rate R_p for the bulk polymerization of styrene at 60°C with Perkadox 16 as initiator: (○) GPC results; (●) \overline{DP} calculated from measurements of limiting viscosity numbers of polystyrenes in toluene at 30°C [20].

velocity constant for initiator decomposition and f is the initiator efficiency. On using the value of Matheson et al. [26] for $k_p/(2k_t)^{1/2}$ in styrene polymerization, $2k_1f$ for Perkadox 16 was $1.33 \times 10^{-4} \text{ sec}^{-1}$ at 60°C . This is higher than the corresponding values of k_1f for AIBN ($1.34 \times 10^{-5} \text{ sec}^{-1}$) and benzoyl peroxide ($5.09 \times 10^{-6} \text{ sec}^{-1}$) in styrene at 60°C [25], and reflects the relative high reactivity of Perkadox 16.

The value of k_1 for Perkadox 16 at 55°C in dichloromethane was $6.6 \times 10^{-5} \text{ sec}^{-1}$ measured directly. The polyperoxides of vinyl chloride had an average first-order decomposition velocity constant k_1 of $8 \times 10^{-5} \text{ sec}^{-1}$ at 55°C in dichloromethane solution, but there appeared to be no acceleration in the rate of polymerization of vinyl chloride at the end of the induction periods produced by added oxygen.

Induction Period Data for Vinyl Chloride-Oxygen in the Presence of Perkadox 16

It is now well established that "tumbled dilatometry" is necessary if induction periods due to oxygen are to be accurately measured for a variety of polymerizing systems [27]. Some typical induction period

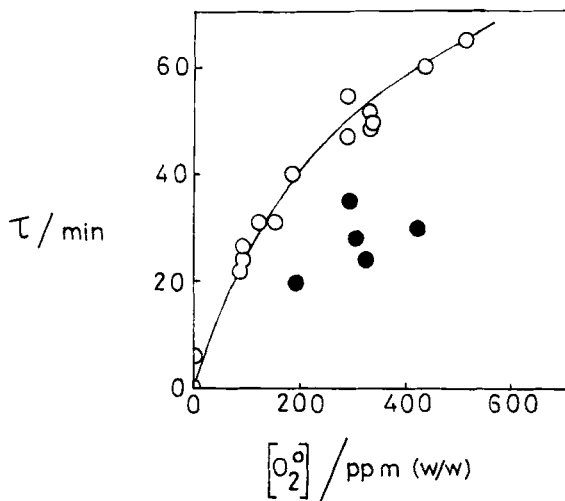


FIG. 3. Induction periods τ for the polymerization of vinyl chloride at 55°C as a function of initial oxygen concentration (ppm w/w): (O) tumbled dilatometry; (●) conventional dilatometry. $[\text{Perkadox 16}] = 0.05 \text{ g/dm}^3$.

results, obtained for vinyl chloride in the presence of Perkadox 16 and various concentrations of oxygen by using both conventional and tumbled dilatometry, are shown in Fig. 3. A thermodynamic treatment of the solubility of oxygen in vinyl chloride indicates that only about 2% of the oxygen would be in the gas phase under equilibrium conditions. Hence the irreproducibility of static dilatometry must be due to the existence of an oxygen-rich phase in the capillary close to the liquid-gas interface. This would not be exhausted by the time that polymerization started in the dilatometer bulbs.

Typical logarithmic plots of the induction periods, determined by tumbled dilatometry, against the logarithm of initial oxygen concentration at constant initial [Perkadox], and against the logarithm of initial Perkadox concentration at constant initial oxygen concentration,

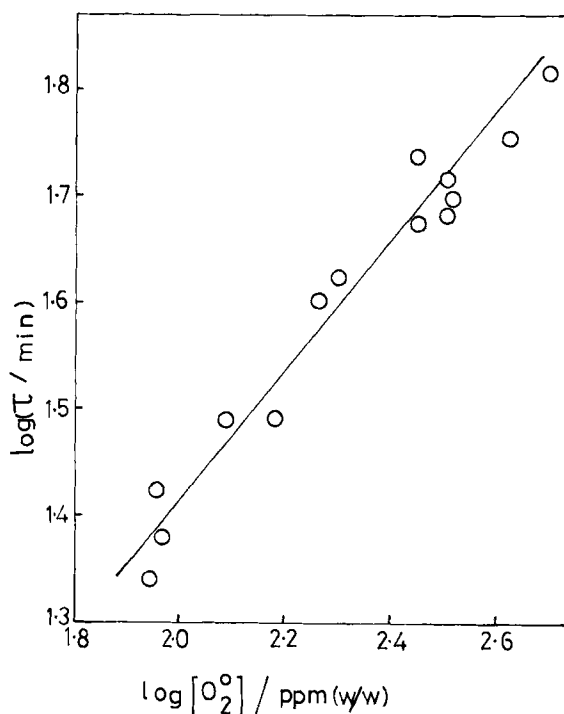


FIG. 4. Plot of \log (induction period) as a function of \log (initial oxygen concentration) for vinyl chloride at 55°C with constant [Perkadox 16] = 0.05 g/dm^3 . Values of τ measured by tumbled dilatometry.

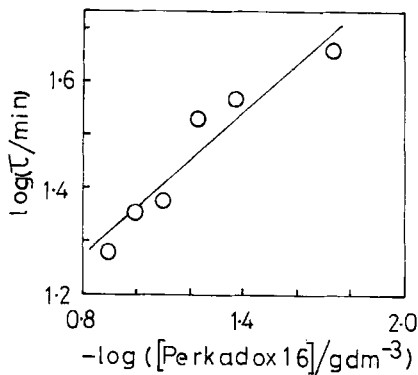


FIG. 5. Plot of \log (induction period) as a function of \log [Perkadox] for vinyl chloride at 55°C with constant $[\text{O}_2] = 160$ ppm (w/w). Values of τ measured by tumbled dilatometry.

are shown in Figs. 4 and 5, respectively. Analysis of the induction period data gave the slope values summarized in Table 1. To a near approximation the induction period data suggest that a conventional oxidation reaction scheme is involved, [1], with a predominant cross-termination reaction between $\text{R}\cdot$ and $\text{RO}_2\cdot$ radicals [Eq. (8)]:

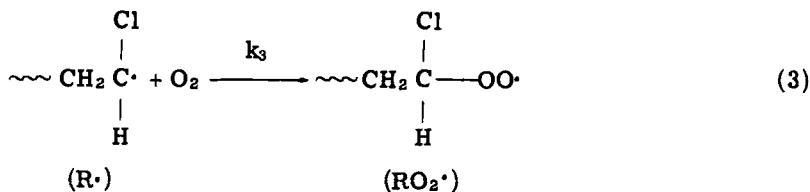
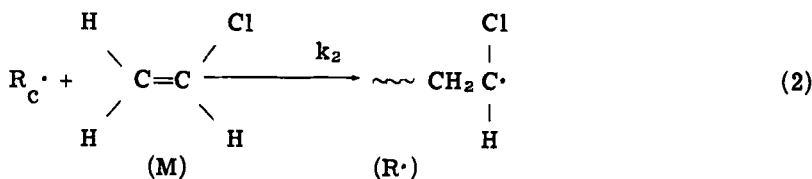
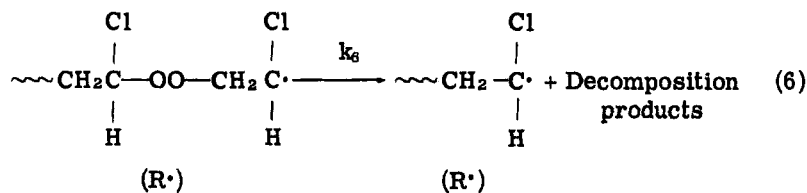
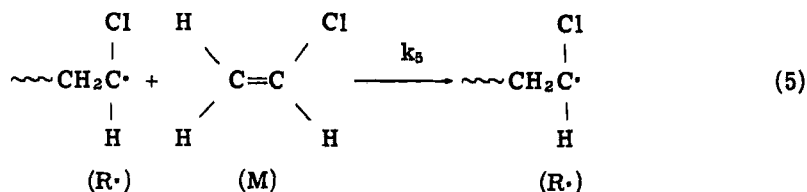
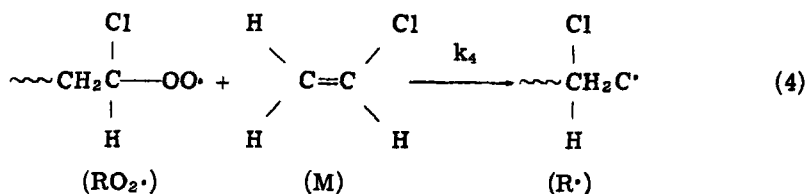


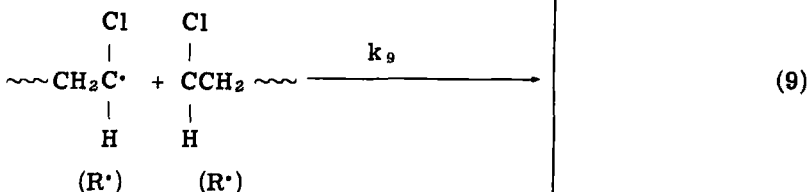
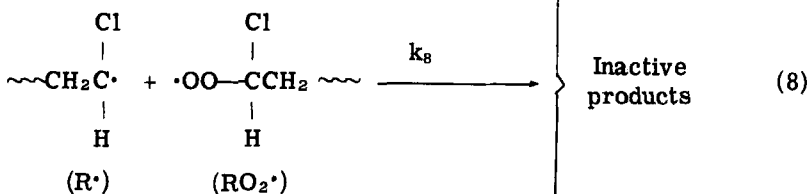
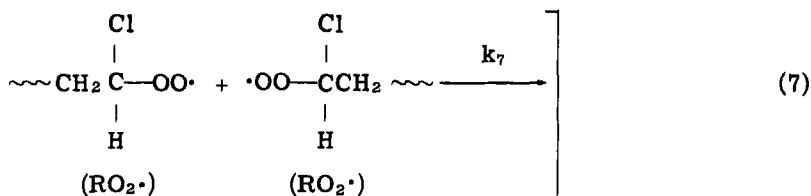
TABLE 1. Analysis of Induction Period Data Obtained by Tumbled Dilatometry for Vinyl Chloride in the Presence of Perkadox 16 and Added Oxygen at 55°C

[Perkadox] (g/dm ³)	Slope	95% Confidence limits
0.050	0.58 ^a	0.06
0.038	0.66 ^a	0.06
0.025	0.53 ^a	0.08
0.019 - 0.128	-0.46 ^b	0.10

^aFrom a plot of $\log \tau$ vs. $\log [O_2^\circ]$ at constant [Perkadox 16].

^bFrom a plot of $\log \tau$ vs. $\log [O_2^\circ]$ plot at constant [Perkadox 16].





In this scheme, In represents the initiator, for example Perkadox 16, and $\text{R}_c\cdot$ is the primary radical from the initiator. Reactions (3) and (4) may be regarded as the main propagation steps in the oxidation when (5) is suppressed, and lead to the formation, after termination, of polyperoxides.

If the decomposition reaction (6) does not interfere with the overall kinetics, and the polyperoxide is relatively inactive as initiator during an induction period, simplifying assumptions [18] lead to the expression for the rate of oxygen consumption:

$$\frac{-d[\text{O}_2]}{dt} = k_4[\text{M}] \left\{ \frac{k_1 f [\text{In}]}{k_9(k_4[\text{M}]/k_3[\text{O}_2])^2 + (k_4 k_8 [\text{M}]/k_3[\text{O}_2]) + k_7} \right\}^{1/2} \quad (10)$$

where f is the initiator efficiency.

With cross-termination as the predominant radical termination mechanism [Eq. (8)], the induction period τ may be found by integration of the expression below between the initial oxygen value $[\text{O}_2^\circ]$ and the value at which homopolymerization occurs, δ .

$$\tau = \int_{\delta}^{[O_2^\circ]} \frac{d[O_2]}{-d[O_2]/dt} = K' [O_2^\circ]^{\frac{1}{2}} [In]^{-\frac{1}{2}} \quad (11)$$

as $\delta \rightarrow 0$, where

$$K' = (4k_8 / f k_1 k_3 k_4 [M])^{\frac{1}{2}} \quad (12)$$

Experimentally, using tumbled dilatometry, it was shown that:

$$\tau = k [O_2]^a [In]^b \quad (13)$$

where k is a constant, $a \sim 0.5$, $b \sim -0.5$, and the monomer concentration is effectively constant. Hence, over the oxygen concentration range investigated, termination occurs predominantly by cross-combination.

Oxidation Products

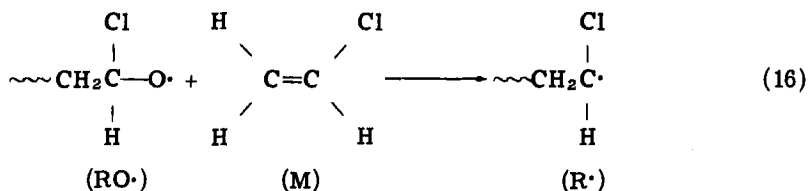
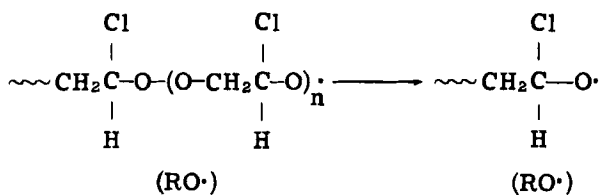
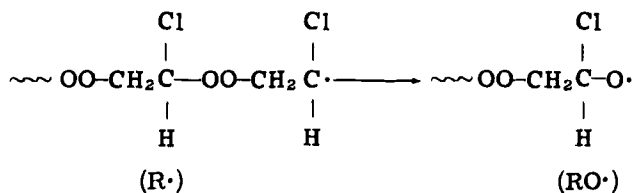
An upper limit of about 30% by weight was found experimentally for the degree of conversion of initial oxygen to peroxidic products [18], with tumbled dilatometry giving about 10% higher conversions than conventional dilatometry. This implies that other oxidation products are formed apart from the vinyl chloride polyperoxides. Gas chromatographic examination of oxidized samples suggested the presence of formaldehyde (HCHO), while gas-phase infrared studies identified carbon monoxide (CO) in the most volatile fraction of the polymerization mixture.

More recently, methanol (CH₃OH) has been identified as an oxidation product formed during an induction period for the vinyl chloride-oxygen-AIBN system, with about 200 ppm w/w of oxygen at 50°C. Following fractionation of the reaction mixture, gas phase samples were injected directly into a low-pressure helium stream within a Pye-Unicam chromatograph fitted with a glass Porapak Q column, (5 ft × 1/4 in.), at 60°C. The chromatograph was interfaced with a helium microwave plasma emission source that was used as a basis for an elemental analyzer [28]. The methanol was identified by means of its empirical formula and its presence checked by injection of samples known to contain methanol.

Low molecular oxidation products have previously been reported for other monomer systems including styrene [11], α -methylstyrene

[12], methyl methacrylate [14], and other unsaturated compounds [29, 30].

For vinyl chloride, polyperoxy radicals with chloroalkyl end groups, $\sim \text{OO}-\text{CH}_2\text{CHCl}$, $\text{R}\cdot$, might decompose to form an epoxide and an $\text{RO}\cdot$ radical by reaction (14). Subsequent radical decomposition of $\text{RO}\cdot$ radicals would predict the formation of HCHO , CO and HCl , two of which were identified.

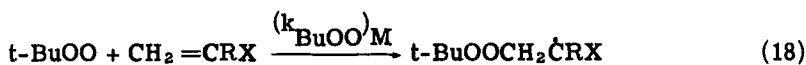


Further evidence for the rapid depolymerization of polyperoxy radicals with chloroalkyl end groups, ($\sim \text{O}-\text{O}-\text{CH}_2\dot{\text{C}}\text{HCl}$), is suggested by the relatively small effect of the peroxide products on the final rate of homopolymerization. Calculations showed that homolytic polyperoxide bond fission with a velocity constant k_1 of $8 \times 10^{-5} \text{ sec}^{-1}$ and a high initiator efficiency f should have produced a threefold increase in the polymerization rate at the end of the induction period for samples of high initial oxygen concentration. Such an effect was not observed. However, f might be low for the polyperoxide, and radical attack on polyperoxide or direct thermal breakdown of the polyperoxide could produce chloroalkyl-ended polyperoxy radicals which could subsequently rapidly depolymerize. Thermal decomposition of vinyl chloride polyperoxide has been shown to produce HCHO, CO and HCl [31].

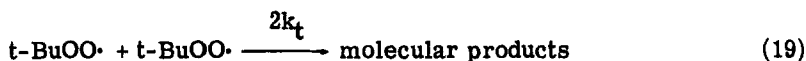
Relative Reactivity of Vinyl Chloride to Oxidation

From the nature of the kinetic scheme already outlined and the form of Eqs. (11) and (12), it is difficult from the present results, at low oxygen pressures, to assess the relative susceptibility of vinyl chloride to oxidation. However, since the earlier studies of monomer oxidation rates by Mayo et al. [32] and Bailey [33] at 50°C , more extensive work at 30°C has been reviewed by Howard [34] which enables the relative reactivity of vinyl chloride to oxidation to be indirectly assessed.

Thus a series of vinyl monomers, $\text{CH}_2=\text{CRX}$, has been oxidized in the presence of tert-butyl hydroperoxide with oxygen pressures > 150 Torr. At hydroperoxide concentrations above about 1 mole/ dm^3 , the rate-controlling propagation and termination reactions are:



and



Measurement of rates of oxidation at known rates of initiation, together with rotating sector methods, enabled absolute values of $(k_{\text{BuOO}})M$ for a series of monomers, M , to be calculated. Now in

the Q-e scheme [34] for defining the reactivity of monomers in copolymerization, the velocity constant, k_{12} , for the addition of monomer 2 to a radical from monomer 1, is given as

$$k_{12} = P_1 Q_2 \exp \{ -e_1 e_2 \} \quad (20)$$

where P_1 is characteristic of the radical 1, Q_2 is a measure of the reactivity of the double bond in monomer 2, while e_1 and e_2 define the polarity of species 1 and 2, respectively. The rate of oxidation of any monomer relative to styrene is equal to the ratio $(k_{\text{BuOO}})_M / (k_{\text{BuOO}})_{\text{St}}$, where $(k_{\text{BuOO}})_{\text{St}}$ is the velocity constant for attack of the radical t-BuOO· on styrene.

Since Q and e are assumed to be 1.0 and -0.8 for styrene, then if e_1 measures the polarity of the t-BuOO· radicals:

$$(k_{\text{BuOO}})_M / (k_{\text{BuOO}})_{\text{St}} = Q \exp \{ -e_1 (e + 0.8) \} \quad (21)$$

or

$$\begin{aligned} \log [(k_{\text{BuOO}})_M / (k_{\text{BuOO}})_{\text{St}}] - \log Q &= Y \\ &= -(e_1 / 2.303)e - (0.8e_1 / 2.303) \end{aligned} \quad (22)$$

Thus the plot of Y against e, for a series of monomers should be linear with a slope of $(-e_1 / 2.303)$ and an intercept equal to $(-0.8e_1 / 2.303)$. Such a least-squares plot is shown in Fig. 6 for rate data at 30°C reported by Howard [34] and currently accepted Q and e values [35] for ten monomers. Collected values are shown in Table 2. From the slope of Fig. 6, the value of e_1 for the t-BuOO· radical is calculated to be +1.98, showing that it is a strongly electrophilic radical. Although the intercept when e is zero is not quite in agreement with the above value of e_1 , the plot indicates that once the general reactivity Q of the monomeric double bond is allowed for, the electrophilic t-BuOO· radical most readily attacks those monomers with an electronegative double bond.

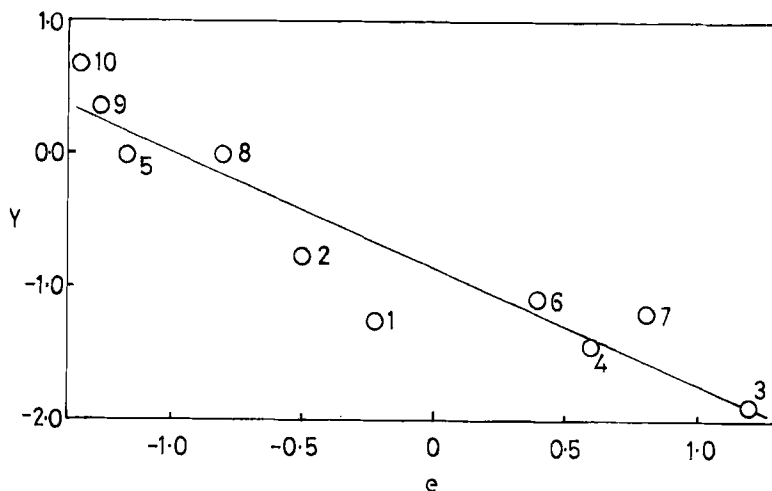


FIG. 6. Plot of $\log [(k_{\text{BuOO}})_M / (k_{\text{BuOO}})_{\text{St}}] - \log Q = Y$ as a function of e for a series of monomers at 30°C . The numbers refer to the monomers in Table 2.

For vinyl chloride, Q and e values are 0.044 and +0.20, respectively. This implies, from Fig. 6, that the velocity constant for the attack of the $t\text{-BuOO}\cdot$ radical on $\text{CH}_2=\text{CHCl}$ is about $5 \times 10^{-3} \text{ dm}^3/\text{mole}\cdot\text{sec}$ at 30°C . Thus vinyl chloride is relatively unreactive to oxidative attack by $t\text{-BuOO}\cdot$ radicals compared with all monomers in Table 2, except for vinyl acetate. According to Howard [34], the absolute velocity constants for autoxidation of vinyl compounds with initiation by $t\text{-BuOO}\cdot$ radicals can be expressed:

$$\log[(k_{\text{BuOO}})_M / \text{dm}^3/\text{mole}\cdot\text{sec}] = 0.0478(E_s / \text{kJ}/\text{mole}) - 4.3 \quad (23)$$

where E_s is the estimated stabilization energy of the β -peroxyalkyl radical, $t\text{-BuOO}\text{CH}_2\dot{\text{C}}\text{RX}$, formed in the addition reaction (18). Using the above value of k_{BuOO} for vinyl chloride, the estimated stabilization energy of $t\text{-BuOOCH}_2\dot{\text{C}}\text{HCl}$, regarded [34] as equivalent to $\text{CH}_3\dot{\text{C}}\text{HCl}$, is about 42 kJ/mole. This low value of E_s , defined in this paper by a difference in bond dissociation energies,

TABLE 2. Autoxidation of Vinyl Compounds in the Presence of tert-Butyl Hydroperoxide at 30°C

No.	Monomer	$(k_{\text{BuOO}})_M$ (dm ³ /mole- sec) ^a	$\log[(k_{\text{BuOO}})_M /$ $(k_{\text{BuOO}})_{\text{St}}]$	Q^b	e^b
1	Vinyl acetate	0.002	-2.8131	0.020	-0.22
2	Isopropenyl acetate	0.01	-2.1140	0.045	-0.50
3	Acrylonitrile	0.01	-2.1140	0.60	1.20
4	Methyl acrylate	0.02	-1.8128	0.42	0.60
5	Ethyl vinyl ether	0.04	-1.5119	0.032	-1.17
6	Methyl methacrylate	0.08	-1.2108	0.74	0.40
7	Methyl acrylonitrile	0.094	-1.1409	1.12	0.81
8	Styrene	1.3	0.0000	1.00 ^c	-0.80 ^c
9	α -Methylstyrene	2.9	0.3485	0.98	-1.27
10	1,1-Diphenylethylene	9.2	0.8498	1.50	-1.35

^aKinetic data from Howard [34].

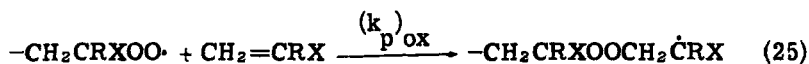
^b Q and e values from Ham [35].

^cAssumed standard values of Q and e .

$$E_S(t\text{-BuOOCH}_2\dot{\text{C}}\text{HCl}) \equiv E_S(\text{CH}_3\dot{\text{C}}\text{HCl}) = D[\text{CH}_3 - \text{H}] - D[\text{CH}_3\text{CHCl} - \text{H}] \quad (24)$$

reflects the low reactivity of vinyl chloride to oxidation. Appropriate bond dissociation energies are reported elsewhere [36].

When vinyl compounds, $\text{CH}_2=\text{CXR}$ [where $\text{R} = \text{CH}_3$ or H and $\text{X} = \text{CN}$, C_6H_5 , $\text{O}(\text{CO})\text{CH}_3$ etc] react with oxygen under the same conditions as described previously, the rate-controlling propagation step becomes



Absolute velocity constants $(k_p)_{\text{ox}}$ for a series of monomers have been determined using rotating sector methods at 30°C, together with values of the velocity constants $(2k_t)_{\text{ox}}$ for mutual termination of the corresponding peroxy radicals. Propagation velocity constants $(k_p)_{\text{ox}}$ are difficult to interpret, due to differences in both peroxyradical and monomer reactivity, and values of $(2k_t)_{\text{ox}}$ also show some variation.

However, for given monomers M, the rates of oxidation at 30°C at constant initiator and monomer concentrations must be proportional to the $[k_p/(2k_t)^{1/2}]_{\text{ox},M}$ values. If $[k_p/(2k_t)^{1/2}]_{\text{ox},\text{St}}$ represents the ratio of kinetic constants for styrene, then application of the Q-e scheme, assuming as a first approximation that all peroxy radicals have the same polarity and reactivity gives:

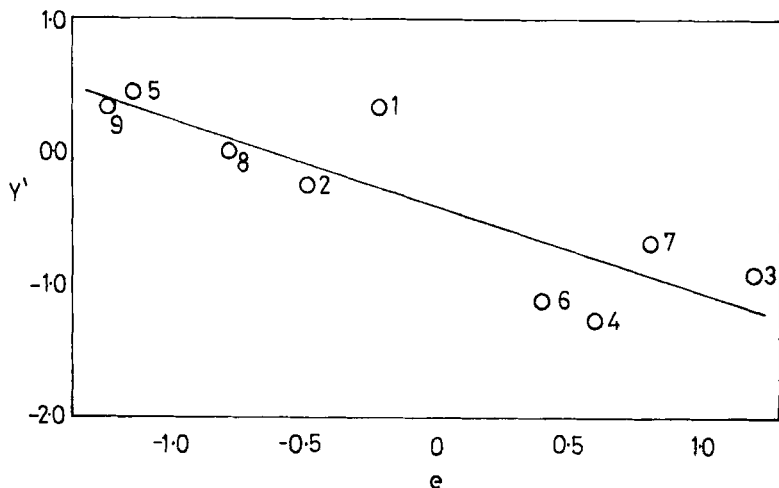


FIG. 7. Plot of $\log \left[\frac{[k_p/(2k_t)^{1/2}]_{\text{ox},M}}{[k_p/(2k_t)^{1/2}]_{\text{ox},\text{St}}} \right] - \log Q = Y'$ as a function of e for a series of monomers at 30°C. The numbers refer to the monomers in Table 3.

TABLE 3. Kinetic Data for the Autoxidation of Some Vinyl Monomers at 30° C

No.	Monomer	$10^3 [k_p / (2k_t)^{1/2}]_{\text{ox}, M}$ ($\text{dm}^3/2/\text{mole}^{1/2} \text{sec}^{1/2}$) ^a	Q ^b	e ^b	Y'
1	Vinyl acetate	0.35 (5) ^c	0.026	-0.22	+0.3359
2	Isopropenyl acetate	0.16	0.045	-0.50	-0.2484
3	Acrylonitrile	0.46(5) ^c	0.60	1.20	-0.9101
4	Methyl acrylate	0.14	0.42	0.60	-1.2764
5	Ethyl vinyl ether	0.56	0.032	-1.17	+0.4437
6	Methyl methacrylate	0.36	0.74	0.40	-1.1122
7	Methyl acrylonitrile	1.48 ^c	1.12	0.81	-0.6783
8	Styrene	6.3	1.00 ^d	-0.80 ^d	0.0000
9	α -Methylstyrene	13	0.98	-1.27	+0.3234

^aKinetic data from Howard [34].

^bQ and e values from Ham [35].

^cMean values.

^dAssumed standard values of Q and e.

$$\frac{[k_p / (2k_t)^{1/2}]_{\text{ox}, M}}{[k_p / (2k_t)^{1/2}]_{\text{ox}, \text{St}}} = \text{rate relative to styrene}$$

$$= Q \exp \{-e_1'(e + 0.8)\} \quad (26)$$

where e_1' represents the average polarity of the radical $-\text{CH}_2\text{CRXOO}\cdot$.

Hence,

$$\log \frac{[k_p/(2k_t)^{1/2}]_{\text{ox},M}}{[k_p/(2k_t)^{1/2}]_{\text{ox},St}} - \log Q = Y'$$

$$= - (e_1'/2.303)e - (0.8e_1'/2.303) \quad (27)$$

A plot of Y' against e for nine monomers is shown in Fig. 7, based on the data in Table 3. From the least-squares slope, the average value of e_1' for the radical $-\text{CH}_2\text{CRXOO}\cdot$ is 1.45, showing that the radical is less electrophilic than the $t\text{-BuOO}\cdot$ radical. This analysis neglects to some extent the known differences in peroxy radical reactivity [33], but permits an estimation of the relative reactivity of vinyl chloride towards oxidation. Thus using the previous values of Q and e for vinyl chloride (VC), $[k_p/(2k_t)^{1/2}]_{\text{ox},VC}/[k_p/(2k_t)^{1/2}]_{\text{ox},St}$ is about 0.013, which means that under identical conditions at 30°C , vinyl chloride would oxidize at about one hundredth the rate of styrene.

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DISCUSSION

Dr. Ugelstad (University of Trondheim, Trondheim, Norway):

Dr. George mentioned earlier work, but not that of Dr. Mørk. He carried out some work on the effect of oxygen in emulsion polymerization, finding about the same effects as Dr. George reported with regard to effects of initiator concentration and oxygen on time of inhibition. The important aspect of Mørk's work was that he showed that the peroxides might reinitiate polymerization if the polymerization was carried out in alkaline solution. At low pH there was no effect on the rate by the peroxides, but increasing the pH led to the peroxides becoming effective initiators. Has Dr. George observed any effects from the addition of amines and so on, in an attempt to obtain the same results as Dr. Mørk?

Dr. George: In my opening remarks I mentioned only the main groups which have worked in this field, but I mentioned also the work of Machacek and Cermak, as well as that of Mørk. Some of their data, either on rate of uptake of oxygen or on induction periods, show some similarity to the results we obtained.

With regard to the other question about the effect of the polyperoxides, on some large-scale suspension polymerization batch reactors we tried to vary the pH to see whether there was an accelerative rate effect. In general, however, there seemed to be little effect of these polyperoxides on the rates of polymerization when the pH was varied. This reinforces our conclusion that if the radicals are able to unzipper, or depropagate, then radicals which can initiate are not being produced. Undoubtedly, it would be expected in alkaline media to find that the polyperoxides would be destroyed quickly. If there is little effect of pH this may be evidence for radical unzipping.

NOTE ADDED IN PROOF

Oxidation side-products similar to those reported in this paper for the bulk system have also been recently reported for the suspension system. [J. Bauer and A. Sabel, Makromol. Chem., **47**, 15 (1975)].