

The Kinetics of Oxidation of Atactic Polystyrene in Solution

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Synopsis

The oxidation of polystyrene initiated by the photodecomposition of 2,2'-azoisobutyronitrile at $\lambda > 300$ nm was studied at 25°C in chlorobenzene solution. The order of the reaction is approximately unity with respect to AIBN concentration and to the light intensity. The effects of concentration and molecular weight on the rate are apparently related to their effects on bulk viscosities of the solutions. The overall kinetics have been interpreted by a general oxidation scheme which incorporates the effect of bulk viscosity on the rate of radical production in the initiation step. Diphenyl alkanes were oxidized under identical conditions and their kinetic parameters are compared with those of the polymer. It would appear that a considerable degree of intramolecular propagation occurs in both systems.

INTRODUCTION

The oxidative and photo-oxidative degradations of polystyrene have been studied repeatedly¹⁻⁴ using solid samples, mainly in the form of thin films. Although these systems bear considerable resemblance to the actual conditions under which oxidative deterioration of the polymer occurs, the gas-solid reaction system is essentially heterogenous, and it is rendered even more complex by concurrent crosslinking reactions. Consequently, it has been difficult to obtain quantitative kinetic information and to deduce reaction mechanisms from such studies. Few studies have been carried out in the liquid phase, and no detailed kinetic information is available for reactions other than for the initiation step associated with the long-wave photo-oxidation of the polymer in solution.^{5,6}

The complications associated with the solid state can be greatly minimized by using the liquid phase, e.g., chain proximities are reduced as are corresponding crosslinking probabilities. A possible disadvantage of the liquid phase is solvent participation; however, it has been shown on numerous occasions that chlorobenzene appears to be an "inert" solvent for oxidation reactions.^{7,8}

The aim of this work was to study the kinetics and mechanism of the liquid-phase oxidation of polystyrene. The reactions were initiated by 2-cyano-2-propyl radicals generated by the photolysis of 2,2'-azobisiso-

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TABLE I
 Properties of Polystyrenes

Polymer	Polym- erization temp., °C	$\bar{M}_n \times 10^{-6}$	$\bar{M}_v \times 10^{-6}$	\bar{M}_v/\bar{M}_n
Anionic	50	0.79	0.94	1.18
Anionic	50	0.325	0.37	1.14
Anionic	50	0.190	0.22	1.15
Anionic	50	0.0445	0.049	1.10
Anionic	50	0.0158	0.019	1.20
Anionic	50	0.0076	0.0092	1.21
Anionic	50	0.0013	0.0016	1.24
Thermal	70	0.94	1.34	1.43
Thermal	50	0.80	1.136	1.42
AIBN Initiated	60	0.201	0.290	1.45
AIBN Initiated	60	0.248	0.368	1.47

butyronitrile (AIBN), this source being used in preference to the thermolysis of AIBN in order to minimize complications arising from the thermal decompositions of hydroperoxide intermediates.⁹

These compounds, however, have generally low extinction coefficients for the long-wave ultraviolet radiation used in this work.¹⁰

EXPERIMENTAL

Materials

Polystyrene. The polymer samples used were either radically or anionically prepared under conditions of rigorous oxygen exclusion. Experimental details have already been published,⁶ but characteristics of the polymers are summarized in Table I.

Chlorobenzene. The B.D.H. sample was purified by washing with dilute sulphuric acid and dried over calcium chloride. It was then distilled (the middle fraction only, bp 132°C being retained) and passed through an activated alumina column before use.

AIBN. The Eastman Kodak sample was recrystallized from ethanol solution, vacuum dried, and stored at -15°C in the dark (mp = 103°C).

Model Compounds. Cumene (Aldrich) and the diphenyl alkanes (Frinton) were distilled through a 1-in. Vigreux column under a nitrogen atmosphere and stored under nitrogen at -5°C. Prior to use they were passed through an activated alumina column.

Measurement of Oxygen Uptake

The progress of the oxidations was followed by differential manometry. The apparatus used was essentially that described previously,¹¹ two Pyrex cells of equal volume being joined by a differential manometer. The solutions underwent oxidation in the cell which contained the photoinitiator, and the other, containing only solution, acted as a compensating volume.

The entire apparatus was immersed in a thermostatically controlled water bath ($\pm 0.05^\circ\text{C}$), and the shaking speed of the solutions in the two cells was maintained at 160 rpm. It was found that the rate of oxygen uptake was independent of shaking speed above about 120 rpm. The AIBN was added to the reaction cell in ether solution by means of a microsyringe, and the solvent was removed under high vacuum. Equal volumes of the polymer solution in chlorobenzene were added to both cells, the solutions were degassed, pure oxygen was then admitted, and the stirring was started. The system was given 30 min to equilibrate before the cells were exposed to the output of a medium pressure mercury lamp (100 W), which had been switched on at least 30 min previously and allowed to stabilize.

The radiation incident on the solutions was restricted to wavelengths of 300 nm and longer by the Pyrex equipment, the principal bands being at 310–316 nm, 320–335 nm, and 360–366 nm. The polymer is transparent to this radiation, but AIBN shows a broad structureless absorption band at the 310–375 nm region. Experiments carried out with filters to isolate these principal bands showed that, within experimental error, the rates of oxidation were independent of the wavelength; and in order to increase the radical flux, the unfiltered spectrum was used throughout this work.

It was established that the Beer-Lambert law applied to the polymer solutions throughout the 310–380 nm region. The total quantum output in this region and the corresponding quantum yield (based on AIBN disappearance) were obtained by a method previously described.¹² A value of 0.49 ± 0.1 for the quantum yield (essentially an average value for the 310–380 nm region) agreed satisfactorily with previous data,¹³ which showed that it is not particularly sensitive to wavelength in this spectral region.

All polymer concentrations are expressed as moles per liter, based on the monomer unit, i.e., the number of tertiary hydrogen atoms in the chain. Except where specified, the oxygen pressure was 600 mm Hg. Rates of oxidation, $-d[\text{O}_2]/dt$, expressed as moles of O_2 absorbed per mole of tertiary hydrogen atom in the polymer per second, were obtained from the observed rate of oxygen absorption, allowance being made for N_2 evolution from the photolysis of AIBN:

$$-d[\text{O}_2]/dt = (-d[\text{O}_2]/dt)_{\text{obs}} + d[\text{N}_2]/dt.$$

Rates of N_2 evolution were determined in the absence of O_2 using the oxidation apparatus and chlorobenzene solutions of the polymer and AIBN.

RESULTS

In order to minimize complications associated with secondary reactions, reaction times were restricted, usually to a maximum of 1 hr.

Figure 1 shows the typically linear oxygen absorption-versus-time data that were obtained. It can be seen that there is no measurable induction period, neither is there evidence of autocatalysis within the reaction period. It can also be seen that the method of polymer preparation has no signifi-

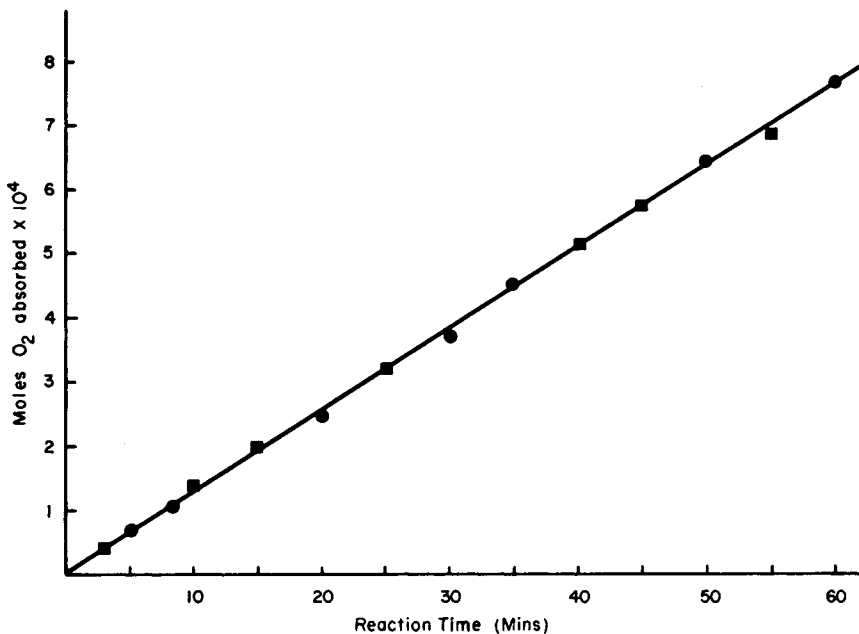


Fig. 1. Photoinitiated oxidation of polystyrene at 25°C. Polymer concentration, 0.8 mole/l.; AIBN concentration, 0.0085 mole/l.; oxygen pressure, 600 mm Hg; (●) free-radical polymer ($\bar{M}_n = 0.201 \times 10^6$); (■) anionic polymer ($\bar{M}_n = 0.190 \times 10^6$); *y*-axis, moles of O₂ absorbed $\times 10^4$; *x*-axis, time of reaction (min).

cant effect on its rate of oxidation, rates of anionically and radically produced polymers with similar molecular weights being indistinguishable.

Effect of AIBN Concentration

Figure 2 shows that the variation of oxidation rate with AIBN concentration, log-log plot, and the initiator exponent, n , in the relationship

$$\text{rate of oxidation} = [\text{AIBN}]^n$$

was found to be 0.93 ± 0.05 for the higher molecular weight polymer ($\bar{M}_n = 0.794 \times 10^6$) and 0.85 ± 0.05 for a lower molecular weight sample ($\bar{M}_n = 9.2 \times 10^5$). While the oxidation rate is apparently a function of molecular weight, the difference in the initiator exponents is not considered to be significant.

Effect of Light Intensity

Light intensities were varied as previously described¹² and corresponding rates obtained.

Figure 3 (log-log plot) summarizes the results, which are qualitatively very similar to those shown in Figure 2. The intensity exponent varies from 0.90 ± 0.05 to 0.99 ± 0.05 with a fivefold variation in molecular

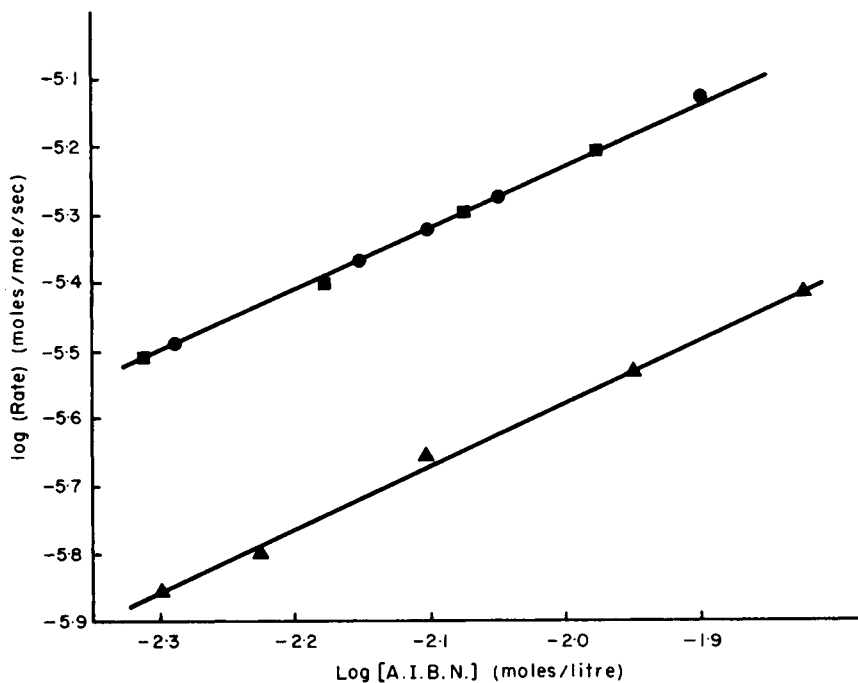


Fig. 2. Rate dependence on AIBN concentration at 25°C. Polymer concentration, 0.75 mole/l.; oxygen pressure, 600 mm Hg; (▲) $\bar{M}_n = 0.79 \times 10^6$; (■) $\bar{M}_n = 0.201 \times 10^6$; (●) $\bar{M}_n = 0.0076 \times 10^6$; y -axis log [rate of oxidation] (moles/mole/sec); y -axis, log [AIBN] (moles/l.).

weight. The difference is not considered to be a significant function of molecular weight.

Effect of Polymer Concentration

Figure 4 shows the variation of rate with polymer concentration. It can be seen that high and low polymers behave differently. For the former class, the linear portion indicates an approximate rate-concentration relation of the form

$$\text{rate} = [\text{PH}]^{0.62}$$

but beyond 0.7 mole/l., the rate becomes independent of concentration and no general relation can be found. For high polymers, the situation is even more complex, with an apparently inverse relationship between rate and concentration. This effect is discussed later.

Effect of Molecular Weight

The rate of oxidation is a function of molecular weight, as shown in Table II. Again, no simple relationship between rate and \bar{M}_n is obvious; however, a plot of rate versus solution bulk viscosity, as shown in Figure 5, is more

TABLE II
Rates of Oxidation as a Function of \bar{M}_n^a

Rate of oxidation, (moles O ₂ /mole polymer/sec) × 10 ⁶	Molecular Weight \bar{M}_n × 10 ⁻⁶
1.82	0.94
2.25	0.80
2.19	0.79
3.87	0.325
4.21	0.248
4.90	0.201
4.82	0.0445
5.14	0.0158
5.05	0.0076
5.11	0.0013

^a Polymer concentration, 0.75 mole/l.; AIBN concentration, 0.0085 mole/l.; temperature, 25°C.

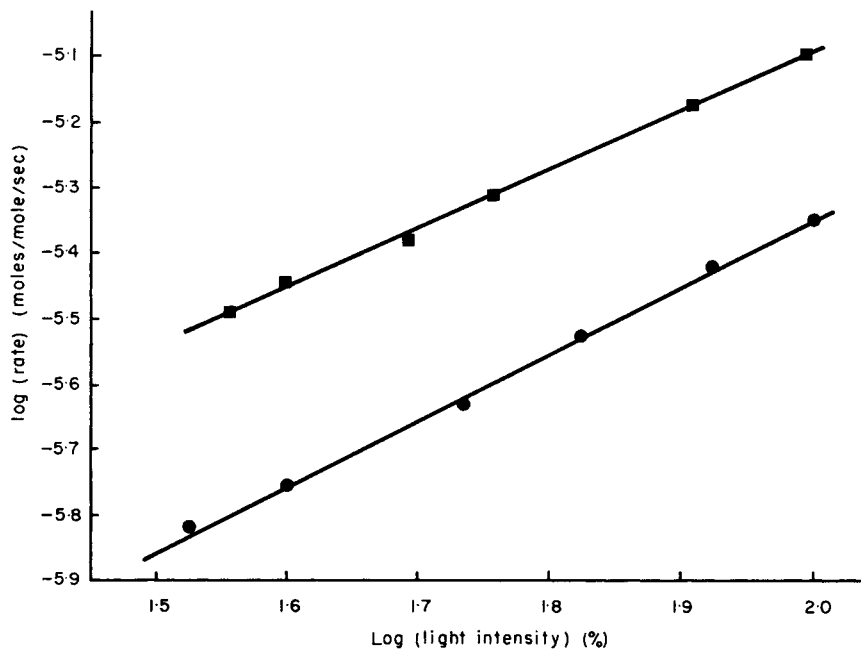


Fig. 3. Rate dependence on light intensity at 25°C. Polymer concentration, 0.8 mole/l.; [AIBN], 0.0085 mole/l.; oxygen pressure, 600 mm Hg; (●) $\bar{M}_n = 0.94 \times 10^6$; (■) $\bar{M}_n = 0.19 \times 10^6$; *y*-axis, log [rate of oxidation] (moles/mole/sec); *x*-axis, log [light intensity] (%).

informative. It can be seen that, while the oxidation rate is approximately independent of viscosity (and molecular weight), at low viscosities the rate falls off significantly beyond molecular weights of $\bar{M}_n = 0.3 \times 10^6$, and it can be concluded that the effect is not related to the molecular weight as such but rather to the solution viscosity associated with a polymer with

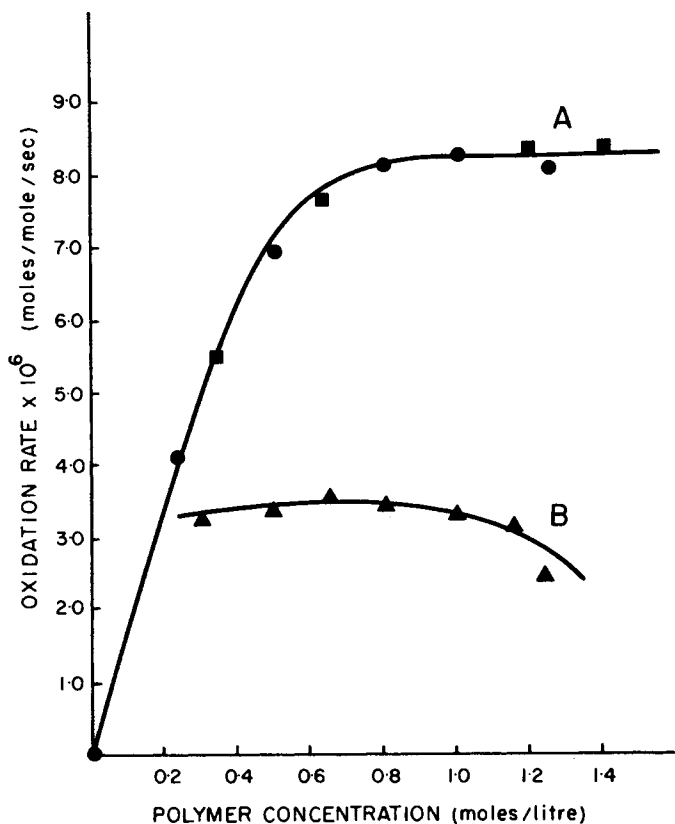


Fig. 4. Rate as a function of concentration at 25°C. Oxygen pressure, 600 mm Hg; [AIBN], 0.013 mole/l.; curve A (low molecular weight samples), (●) $\bar{M}_n = 0.0076 \times 10^6$ and (■) $\bar{M}_n = 0.190 \times 10^6$; curve B (high molecular weight), (▲) ($\bar{M}_n = 0.94 \times 10^6$; y -axis, rate of oxidation $\times 10^6$ (moles/mole/sec); x -axis, polymer concentration (moles/l.).

a given value of \bar{M}_n (or \bar{M}_v). The polydispersity of the samples appears to have no significant effect on rates, narrow-distribution anionic polymers being similar to wider-range free-radically produced polymers.

The unexpected behavior of the high molecular weight polymer shown in curve B, Figure 4, is perhaps also a function of increasing bulk viscosity.

Oxygen Pressure

Reactions were carried out over an oxygen pressure range of 150–750 mm Hg. The results shown in the Table III demonstrate that above about 350 mm Hg, the rate is independent of O₂ pressure. Similar results were obtained for model compounds and low and high molecular weight polymers.

TABLE III
Effect of Oxygen Pressure on Oxidation Rate at 25°C^a

Oxygen pressure, mm Hg	Rate of oxidation, (moles O ₂ /mole/sec) × 10 ⁶	
	$\bar{M}_n = 0.201 \times 10^6$	$\bar{M}_n = 0.79 \times 10^6$
150	5.94	2.40
250	6.54	2.47
350	6.74	2.51
450	6.58	2.50
550	6.67	2.52
650	6.64	2.51
750	6.60	2.50

^a Polymer concentration, 0.75 mole/l.; AIBN concentration, 0.008 mole/l.

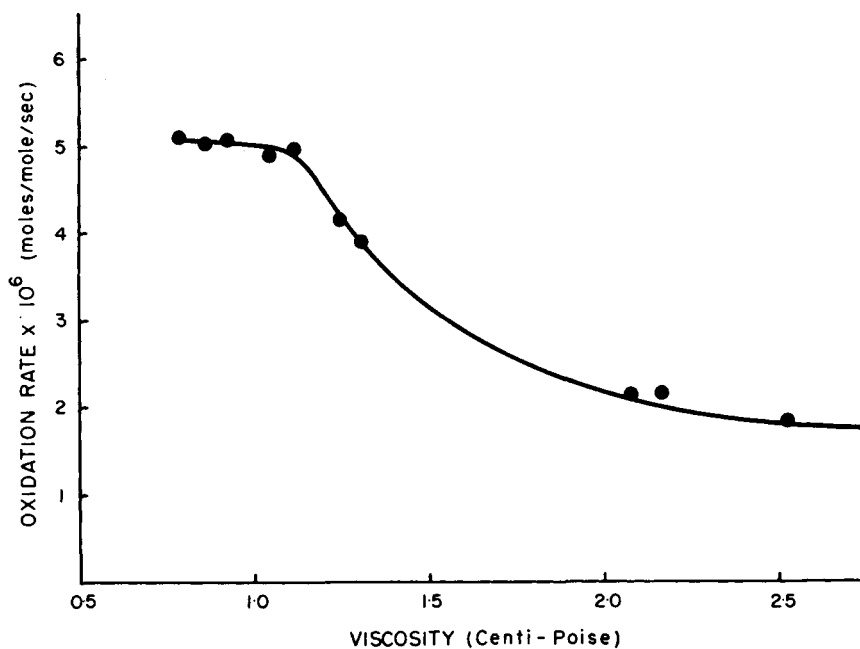


Fig. 5. Rate as a function of bulk viscosity at 25°C. Polymer concentration, 0.95 mole/l.; [AIBN], 0.0085 mole/l.; oxygen pressure, 600 mm Hg; *y*-axis, rate of oxidation × 10⁶ (moles/mole/sec); *x*-axis, viscosity (centipoises).

Kinetic Parameters

Oxidations were carried out over the temperature range of 20°–60°C, and activation energies were determined. Corrections were applied for the “thermal” contribution to the initiation, using the unimolecular decomposition rate expression¹⁴

$$k_1 = 1.78 \times 10^{15} \exp(-31000/RT)$$

TABLE IV
 Oxidation of Polystyrene and Model Compounds—Kinetic Parameters*

Compound	Chain length (25°C)	Activation Energy E (overall), (kcal/mole)	A Factor A (overall)	AIBN exponent (25°C)	Intensity exponent (25°C)	Hydrocarbon concentration exponent (25°C)
Cumene	23	6.5 ± 0.3	147	0.51	0.52	0.98
1,3-Diphenylpropane (1)	9	8.1 ± 0.3	28	0.59	0.56	0.94
1,3-Diphenylbutane (2)	6	7.8 ± 0.3	16	0.64	0.61	0.87
2,4-Diphenylpentane (3)	4	7.4 ± 0.3	11	0.68	0.65	0.81
Polystyrene ($\bar{M}_n = 9.2 \times 10^3$)	2.4	9.3 ± 0.4	4	0.85	0.92	0.62
Polystyrene ($\bar{M}_n = 8 \times 10^5$)	1.5	12.9 ± 0.5	—	0.94	0.98	—

* Concentrations, 0.68 mole/l., [AIBN], 0.013 mole/l.; solvent chlorobenzene; oxygen pressure 600 mm Hg.

The overall activation energy varies with molecular weight, lower polymers ($\bar{M}_n < 10^5$) having a typical value of 9.3 ± 0.5 kcal/mole and the highest polymer studied ($\bar{M}_n = 0.94 \times 10^6$) having a value of 12.9 ± 0.5 kcal/mole.

Kinetic chain lengths were obtained by comparing oxidation rates with rates of AIBN decomposition. Since it has been established that the initiation efficiency of AIBN is dependent on the bulk viscosity^{15,16} of the solution in which it is being decomposed, it was necessary to obtain the actual initiation efficiency of AIBN in each of the solutions studied.

This was determined using 2,5-di-*tert*-butylmethylphenol as inhibitor by a method previously described.¹⁷ Typical initiation efficiencies are as follows (all compounds in equimolar chlorobenzene solutions): cumene, 0.58 (in good agreement with Bawn's data⁸); 2,5-diphenylpentane, 0.57; polystyrene ($\bar{M}_n = 1300$), 0.55; polystyrene ($\bar{M}_n = 4.54 \times 10^4$), 0.43; polystyrene ($\bar{M}_n = 9.4 \times 10^5$), 0.39.

Chain lengths for polystyrene oxidation are similar to those for polypropylene⁸ and are apparently molecular weight dependent, with a value of 1.8 for the highest ($\bar{M}_n = 9.4 \times 10^5$) and 2.8 for the lowest ($\bar{M}_n = 1300$) polymers, respectively. However, there appears to be no simple relationship between chain length and \bar{M}_n .

Kinetic data are summarized in Table IV. Because of the complex nature of the rate expression for the high polymers, the frequency (A) factor and the polymer concentration exponent are not readily available, and are omitted from the table. It should also be noted that at higher concentrations, the low polymers have rates which are independent of the polymer concentration.

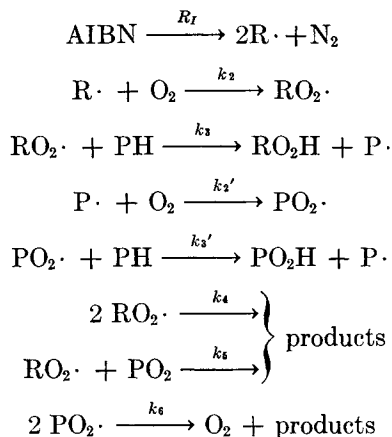
Oxidation of Model Compounds

Cumene and diphenyl alkanes were oxidized under identical conditions, the diphenyl alkanes being considered more appropriate structural models for the polymer. The close similarity of the kinetic results for cumene with those obtained previously by a number of different techniques^{1,7,18} indicates that the present experimental technique was not responsible for the unexpected rate expressions obtained for the polymer; e.g., for cumene, the overall rate constant, $k_p/2k_t^{1/2}$, has a value of 15.2×10^{-4} (l. mole⁻¹ sec⁻¹)^{1/2} at 30°C, compared with Ingold's value of 15.0×10^{-4} obtained at the same temperature.⁷

Kinetic data for model compounds are shown in Table IV.

DISCUSSION

The AIBN-initiated oxidation of hydrocarbons may be represented by the following scheme¹⁹ in which radicals derived from AIBN and the hydrocarbon (PH) possess different reactivities, and oxygen produced in the termination step is derived from the hydrocarbon peroxy radicals only:



The rate of oxidation is

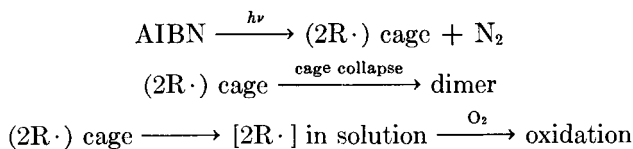
$$-\frac{d[\text{O}_2]}{dt} = k_2(\text{R}\cdot)(\text{O}_2) + k_2'(\text{P}\cdot)(\text{O}_2) - \frac{k_6}{2}(\text{PO}_2\cdot)^2 \quad (1)$$

and using the usual steady-state assumptions with respect to each radical, it can be shown that, in the concentration range studied throughout this work, the rate (R_o) is given by the expression

$$R_o = \frac{k_3(\text{PH})R_I^{1/2}}{k_6^{1/2}} + \frac{3}{2}R_I \quad (2)$$

Equation (2) is qualitatively very similar to that derived by Bawn⁸ using a simpler kinetic scheme.

The following steps are involved in the initiation of oxidation:



The effective rate of initiation is

$$R_I = \frac{d[\text{R}\cdot]}{dt} = 2\Phi\epsilon I_0(1 - e^{-\mu l[A]}) \quad (3)$$

in which ϵ is the initiation efficiency ($\epsilon < 1$, because cage collapse reactions restrict the number of radicals available for initiating oxidation); I_0 is the incident light intensity; μ is the extinction coefficient; l is the depth of solution (light path); $[A]$ is the AIBN concentration; and Φ is the quantum yield. Since the amount of light absorbed by the AIBN solutions is small (typically, $\mu = 13.5$ [average value for the 310–370 nm region], $l = 0.4$ cm, and $[A] = 8 \times 10^{-3}$ mol/l.,

$$1 - e^{-\mu l[A]} = \mu l[A]$$

and

$$R_I = 2\Phi\epsilon I_0 \mu l[A] \quad (4)$$

$$= 2\xi I_0[A]\epsilon \quad (\xi = \Phi\mu l) \quad (5)$$

Hence, oxidation rate (R_o) from eq. (2) becomes

$$R_o = \frac{k_3(\text{PH})(2\xi I_0[A]\epsilon)^{1/2}}{k_6^{1/2}} + 3\xi I_0[A]\epsilon. \quad (6)$$

Making allowance for N_2 evolution from AIBN, the observed rate is

$$R_o' = \frac{k_3(\text{PH})(2\xi I_0[A]\epsilon)^{1/2}}{k_6^{1/2}} + \xi I_0[A](3\epsilon - 1) \quad (7)$$

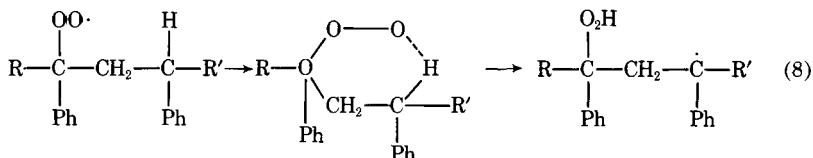
where the rate of N_2 evolution is $\xi I_0[A]$. It has been established that for compounds like cumene,¹⁹ the first term in eq. (7) greatly exceeds the second, and the rate expression simplifies to

$$R_o' \propto (I_0)^{1/2}[A]^{1/2}(\text{PH}). \quad (7')$$

Table IV shows that eq. (7) is borne out for cumene; however, the diphenyl alkanes show progressive deviations from (7'), and (7') is not applicable to polystyrene. It can also be seen (Table IV) that all of these compounds have correspondingly shorter chain lengths (than cumene), presumably because of the higher activation energies for their propagation steps, and it is no longer justifiable to ignore the second term in eq. (7). Thus, the values of catalyst and intensity exponents greater than 0.5 for (1) and (2) and (3) can be accounted for.

If eq. (6) is valid, however, a hydrocarbon concentration exponent of 1.0 is expected, and it is likely that the lower observed values for model

compounds and polymers are associated with propagation steps involving both inter- and intramolecular H abstraction. The intramolecular reaction may be written as follows:



The activation energies (E) for the inter- and intramolecular reactions should be comparable for a given compound, the actual magnitude depending on the dissociation energy of the C—H bond from which the H is abstracted. The variation of E from compounds (1) to (3) (Table IV) reflects the relative ease of abstraction from tertiary substituted C atoms. The higher values for polymers are probably the result of steric inhibition of resonance stabilization of the P· type radicals.

The overall rates and chain lengths decrease from compound (1) to compound (3) and are even lower for polymers; and it would appear (Table IV) that the lower A factors compensate to some extent for the E values for compounds (1) to (3) and depress reaction rates for polymers. Since A factors can be identified with entropies of activation, ΔS^\ddagger , $A = \exp(\Delta S^\ddagger/R)$, it follows that the A factor for the intramolecular reaction will be less than that for the intermolecular reaction involved in cumene oxidation, formation of the six-membered cyclic intramolecular transition state being accompanied by a greater loss of rotational and vibrational degrees of freedom and hence by a greater entropy decrease.

The correlation between A and the decreasing hydrocarbon exponent probably indicates greater participation of the intramolecular process; however, the polymer geometry will undoubtedly impose restrictions on the structures and mobilities of transition states for both processes, and lower A factors will result. It is therefore not possible to state unequivocally that the propagation step in polystyrene oxidation is predominantly intramolecular. In addition, the overall rates of these reactions can be influenced by termination reaction rates; in particular, it would appear that the combination of two peroxy radicals becomes less probable as the molecular complexity increases.

The overall kinetic expressions for the polymer are complex. No single expression is valid over the complete concentration or \bar{M}_n range studied; however, both intensity and AIBN exponents tend to be close to unity.

Since the propagation rates and chain lengths for polymers are low, the second term in eq. (6) assumes greater importance relative to the first, and this effect can be enhanced if the evolution of O_2 in the termination step involving two polymer peroxy radicals is sufficiently small to be ignored.

Equation (6) then becomes

$$R_o = \frac{k_3(\text{PH})(2\xi I_0[A]\epsilon)^{1/2}}{k_6^{1/2}} + 4\xi I_0[A]\epsilon \quad (9)$$

In the limit when the first term becomes negligible, the overall rate of oxidation is dependent on the rate of photodecomposition of AIBN, i.e.,

$$R_o \propto I_0[A]\epsilon. \quad (10)$$

With the exception of lower- \bar{M}_n polymers in more dilute solution ($c < 0.7$ mole/l.), polystyrene oxidation conforms to eq. (10). The lower exponents observed for low polymers in dilute solution (Table IV) can be more appropriately represented by (9). Equation (10) may also be used to rationalize the effects of \bar{M}_n and concentration on rates, i.e., (a) high- \bar{M}_n polymers at low and moderate concentrations ($c < 1$ mole/l.) and low polymers at moderate concentrations ($c < 1$ mole/l.) have rates $\propto (\text{PH})^0$ (b) high- \bar{M}_n polymers in more concentrated solutions have rates $\propto (\text{PH})^x$, where $x < 0$. (c) Dilute solutions of low polymers ($c < 0.7$ mole/l.) have rates $\propto (\text{PH})^{0.6}$.

(a) Equation (10) predicts an independence of rate and polymer concentration. (A large degree of intramolecular propagation would give a similar result.)

(b) Both concentration and \bar{M}_n contribute to solution bulk viscosity (η), which in turn has been shown to influence ϵ in the following approximate manner¹⁵:

$$\frac{1}{1 - \epsilon} = \alpha + \frac{\beta}{\eta} \quad (11)$$

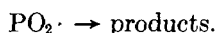
where α and β are constants. Different forms of eq. (11) have been suggested for other polymer systems, and it would appear that the exact quantitative relation between ϵ and η is complex.¹⁶

Combining eqs. (10) and (11), it can be seen that, as η increases, the extent of the cage effect for AIBN dissociation increases, with a consequent diminution in ϵ and hence in the rate of oxidation. The results in Figure 5 can be qualitatively interpreted in similar terms. However, since ϵ is not simply related to $1/\eta$, the effect on the rate does not become apparent until appreciable viscosities are involved.

It has also been suggested that a portion of the radicals from the AIBN decomposition that have escaped from the cage are subject to deactivation by bimolecular combination reactions.²⁰ Since this effect will be enhanced by increasing viscosity, it will reinforce that discussed above. The apparently anomalous relations between rate and concentration and \bar{M}_n can be better ascribed to physical than to chemical effects.

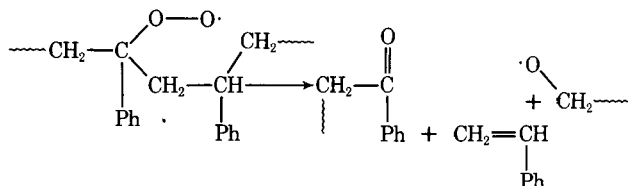
(c) The exponent of 0.6 is difficult to explain in terms of any one equation shown above, particularly since the kinetic chain lengths are small (< 3). However, it is possible that it reflects a degree of intramolecular propagation, but the relation becomes less valid as the effect of bulk viscosity increases.

Intensity and AIBN exponents of unity could conceivably also be indicative of a first-order termination step, such as



However, it has been observed that tertiary peroxy radicals derived from hydrocarbons have appreciable stabilities and react predominantly by bimolecular processes,¹⁷ and a bimolecular termination step appears to be significant in the solution oxidation of polypropylene.⁸ It would therefore seem unlikely that the polystyrene peroxy radical would react exclusively by a first-order process.

Chemical instability of polystyrene $\text{PO}_2\cdot$ radicals has been invoked to account for the products of the radiolytic/oxidative degradation,^{22,23} the $\text{PO}_2\cdot$ decomposing intramolecularly as follows:



The styrene reacts further to yield epoxystyrene, benzaldehyde, etc.

No evidence was obtained in the present study for any of these products, despite the fact that apart from the γ -radiation the systems were similar; and it is suggested that the unimolecular breakdown of $\text{PO}_2\cdot$ may be related to the γ -irradiation of the system. It is concluded that such a unimolecular decomposition is not significant under the present conditions. An apparent first-order termination step could be the result of the physical characteristics of the system.

Viscosities of polystyrene solutions were considerably higher than those of the hydrocarbons, and diffusion rates of $\text{PO}_2\cdot$ radicals will be correspondingly lower. However, it is unlikely that the viscosity of any solution used in this work is sufficiently high to immobilize $\text{PO}_2\cdot$ radicals to such an extent as to preclude bimolecular collisions. The termination step is perhaps diffusion controlled at higher viscosities, but it has been established²¹ that even at the much higher viscosities encountered in bulk polymerization, macroradicals still undergo bimolecular termination reactions.

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