Translated from *Uspekhi Khimii*, 47, 1090-1118 (1978) U.D.C. 541.64 : 542.952

Solid-phase Radical Reactions and Mechanism of Oxidation of Carbon-chain Polymers

E.T.Denisov

Analysis of recent results on the kinetics of the oxidation of model hydrocarbons and carbon-chain polymers in solution and in the solid phase emphasises the common character of the oxidation mechanisms in liquid and solid phases. Detailed consideration is given to specific features of the solid-phase oxidation of polymers consequent on their high molecular mass, inhomogeneity in the solid state, the influence of molecular mobility on the kinetics of radical reactions, and the migration of free electrons. A list of 104 references is included.

CONTENTS

I.	Introduction	572
II.	Oxidation of polymers in solution	572
III.	Reactivity of polymers and model hydrocarbons	574
IV.	Similarity of the mechanisms of oxidation of liquid hydrocarbons and solid polymers	575
V.	Primary radical reaction in a polymer matrix	576
VI.	Chain generation and propagation	577
VII.	Relay mechanism of migration of a free electron in a polymer	579
VIII.	Reactions of alkyl macroradicals in polymers undergoing oxidation	581
IX.	Formation and breakdown of hydroperoxy-groups	582
X.	Conclusion	584

I. INTRODUCTION

The history of science contains many examples of how, with the development of theory and experiment, research workers pass from studying comparatively simple to increasingly complicated systems, a tendency that can be traced in the kinetics of chain oxidations. Semenov's theory of branched and degenerate chain reactions was based on the gas-phase oxidation of simple molecules[1]. The oxidation of hydrocarbons and aldehydes in the gas phase occupied a central position in kinetic research during the 1930s and 1940s.[2] Advance into the liquid-phase oxidation of hydrocarbons was a feature of kinetic investigations during the 1950s,[3] which was subsequently applied to diverse organic compounds[4]. During the past decade the interest taken by research workers in the mechanism of the oxidation of polymers has grown considerably, both in our own country[5,6] and abroad[7-9]. The number of publications devoted to oxidation and radical reactions in polymers approaches the number on liquid-phase oxidation and far exceeds the annual number on gas-phase oxidation. Some of the apparent reasons for this change in the direction of research are enumerated below.

Firstly, the theory of the oxidation of polymers forms the scientific basis for their stabilisation and for predicting the durability of polymeric materials.

Secondly, the oxidation of polymers relates to a complicated, interesting, and hitherto largely unsolved scientific problem—the kinetics of radical reactions in the solid phase—and thus to the radiation chemistry of polymers and solid-phase polymerisation.

Thirdly, quantitative kinetic methods, developed earlier in the study of the liquid-phase oxidation of hydrocarbons, have been more and more widely used in research on the oxidation of polymers. Results obtained by these methods permit in several cases a quantitative comparison with the liquid-phase oxidation of model hydrocarbons.

Fourthly, very valuable results have recently been obtained on the oxidation of polymers in solution. Electron spin resonance has been widely used to measure the rate constants of radical reactions[10,11]. It has revealed the polychromatic kinetics of radical reactions in the solid phase[11] and the dependence of the rate of the primary step on the rigidity of the polymer matrix[12].

Comparison of experimental results obtained during recent years on the oxidation of polymers with data on the liquid-phase oxidation of model hydrocarbons indicates the similarities and differences between solid-phase and liquid-phase oxidation, together with possible reasons for such differences. These aspects will be covered in the present Review.

II. OXIDATION OF POLYMERS IN SOLUTION

The liquid-phase chain oxidation of hydrocarbons[3] and other organic compounds[4] involves the following primary stages

$$\text{Initiation } \text{In} \xrightarrow{k_i} \text{r}^{\cdot} \xrightarrow{RH} R^{\cdot} \qquad (i)$$

$$\text{Chain progagation } R^{\cdot} \xrightarrow{O_2} RO_2^{\cdot} \xrightarrow{RH} ROOH + R^{\cdot} \qquad (1, 2)$$

$$\text{Self-initiation } ROOH \rightarrow \text{Free radicals } (R^{\cdot}) \qquad (3)$$

$$\text{Chain termination } R^{\cdot}(RO_2^{\cdot}) + R^{\cdot}(RO_2^{\cdot}) \rightarrow \text{Molecular products} \qquad (4-6)$$

With a practically constant rate of initiation, when $k_1[\text{In}] \gg k_3[\text{ROOH}]$, and a sufficiently high concentration of dissolved oxygen ($k_1[O_2] \gg k_2[\text{RH}]$) the rate of liquid-phase oxidation is described by a formula which for long chains becomes

$$W_{O_2} = a[\text{RH}]\, W_i^{1/2},$$

where W_i is the rate of initiation. The reason for the first order with respect to RH is that chain propagation is limited by the reaction $RO_2^{\cdot}$ + RH, the order 0.5 with respect to the initiator is due to bimolecular (quadratic)

chain termination, and the zero order with respect to oxygen is connected with preferential chain termination by reaction (6) between two peroxy-radicals. At low RH concentrations the oxidation chains are short, so that absorption of oxygen must be taken into account even in the act of initiation, and the rate of such absorption in the steady state is

$$W_{O_2} = 1/2W_i + a[RH]\cdot W_i^{1/2}, \quad a = k_2\cdot k_6^{-1/2}.$$

This formula is valid for peroxide initiators, such as cumenyl, t-butyl, and benzoyl peroxides, whose decomposition yields alkoxy- or acyloxy-radicals that do not react with oxygen but attack the hydrocarbon. When initiators that generate alkyl radicals are used, such as azoisobutyronitrile, reaction of the initiator radical $r^\cdot$ with oxygen

$$r^\cdot \xrightarrow{O_2} rO_2^\cdot \xrightarrow{RH} R^\cdot + rOOH$$

must also be taken into account, so that

$$W_{O_2} = 3/2W_i + a[RH]\cdot W_i^{1/2}.$$

With sufficiently long chains $W_{O_2} \simeq [RH]W_i^{1/2}$: i.e. the reaction has the first order with respect to the hydrocarbon, and 0.5 with respect to the initiator, in agreement with experimental results (Table 1, cumene).

The equation of the above type for polymers PH in solution is [13]

$$W_{O_2} = 2W_i + a[PH]\cdot W_i^{1/2},$$

For the oxidation of polystyrene in the presence of azoisobutyronitrile in benzene and in chlorobenzene a is respectively 3.6×10^{-4} and 5.0×10^{-4} $M^{-1/2}\,s^{-1/2}$ at 333 K (activation energy $E = 74.2$ kJ mole^{-1}). The solvent may take part in the oxidation, which is apparently why the coefficient of W_i is 2, not $1\frac{1}{2}$, while the coefficient a has different values in the two solvents. Table 1 shows that the dependence of the rate of the initiated oxidation of polyethylene, polypropylene, and polystyrene on the initiator and polymer concentrations differs from the corresponding relation for a hydrocarbon [Eqns. (I) and (II), and data for cumene in Table 1]: the order with respect to the initiator always exceeds 0.5 and is close to unity. The first order has been established for polyethylene and polypropylene in chlorobenzene [14], which indicates the linear character of chain termination in the oxidation of polymers in solution. This is because the recombination of two peroxy-macroradicals $PO_2^\cdot$ in solution takes place slowly owing to the slowness of the diffusion of one coiled macromolecule into another, so that chain termination results from reaction between a macroradical and molecules of low molecular weight arising from attack by radicals on solvent molecules.

Chlorobenzene is not absolutely inert [14], but slowly oxidises when cumenyl peroxide decomposes. Its rate of oxidation is described by Eqn. (I) with the coefficient $a = 3.85 \times 10^5 \exp(-68/RT)$. Oxidation is due to the ability of aromatic molecules to add radicals with subsequent generation of $HO_2^\cdot$ and $HO^\cdot$:

$$ROOR \rightarrow 2RO^\cdot$$
$$RO^\cdot + ArH \rightarrow ROArH$$
$$ROArH + O_2 \rightarrow ROAr + HO_2^\cdot$$
$$HO_2^\cdot + ArH \rightarrow ArOH + HO^\cdot$$
$$HO^\cdot + ArH \rightarrow HOArH$$
$$HOArH + O_2 \rightarrow ArOH + HO_2^\cdot.$$

When a polymer is oxidised in such a solvent, the $HO_2^\cdot$ radicals diffuse rapidly and react with $PO_2^\cdot$, thus effecting chain termination, the rate of which is directly proportional to the rate of reaction of $RO^\cdot$ with the solvent, i.e. the rate of initiation W_i. The order of oxidation with respect to the polymer is always less than unity (Table 1); for polystyrene of number-average molecular mass 100 000 the kinetic order is zero [18].

When azoisobutyronitrile (AIBN) is used as initiator, it is improbable that 1-cyano-1-methylethylperoxy-radicals formed from the initiator in the presence of oxygen will attack the solvent (benzene) molecules. At low polymer (PH) concentrations in such systems (ArH–[CN.C(CH$_3$)$_2$.N:]$_2$–O$_2$–PH) a peroxy-radical of the initiator apparently reacts with the peroxy-macroradical. At sufficiently high PH concentrations $HO_2^\cdot$ radicals, formed after $RO^\cdot$ and $HO^\cdot$ radicals appearing in the system have interacted with the solvent, may be involved in termination.

The primary reason for the diminished order with respect to the oxidisable compound on passing from a hydrocarbon to a polymer is that oxidation in the latter takes place predominantly within each coiled macromole-

Table 1. Kinetics of the oxidation of polymers in solution (I = light intensity).

Polymer	Solvent	Initiator	T, K	[PH] or [RH], M	Rate of oxidation	Chain length	Ref.
Polyethylene	C_6H_5Cl	cumenyl peroxide	391	0.1—3	$[In]\cdot[PH]^{0,37}$	1—4	14
Isotactic	C_6H_5Cl	cumenyl peroxide	384	0.1—1.3	$[In]\cdot[PH]^{0,55}$	2—9	14
polypropylene	C_6H_6	t-butyl peroxide	373—403	0.8—4.0	$[In]^{0.85}\cdot[PH]^{0,73}$	7—30	15
Atactic	$C_6H_3Cl_3$	AIBN	353—373	2.05—0.25	$[In]^{0,85}\cdot[PH]^{0,37}$	—	16
polypropylene	$C_6H_3Cl_3$	AIBN	353—373	0.25—1.50	$[In]^{0,85}\cdot[PH]^{0,12}$	—	16
Polystyrene	C_6H_5Cl	AIBN	333	0.05—0.88	$[In]^{0,5}\cdot[PH]^{0,34}$	1	17
$\bar{M}_n = 10^4$	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[In]^{0,85}\cdot I^{0,92}\cdot[PH]^{0,62}$	2.4	18
$\bar{M}_n = 10^5$	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[In]^{0,94}\cdot I^{0,98}\cdot[PH]^{0}$	1.5	18
Cumene	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[In]^{0,51}\cdot I^{0,52}\cdot[RH]^{0,98}$	23	18
2,4-Diphethylpentane	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[In]^{0,68}\cdot I^{0,65}\cdot[RH]^{0,81}$	4	18

*AIBN = azoisobutyronitrile.

cule. As soon as all the initiator radicals have reacted with the polymer to form P$^{\cdot}$ radicals (for which a minimum concentration $[PH]_{min}$ is required), further oxidation as a sequence of steps (1) and (2) takes place within a single macromolecule, resulting in a lower order of oxidation with respect to the polymer. Comparison of the photoinitiated oxidation of cumene, 2,4-diphenylpentane, and polystyrene (Table 1) leads to the same conclusion: whereas for cumene the kinetic order with respect to PH is unity, diphenylpentane undergoes appreciable intramolecular isomerisation of $RO_2^{\cdot}$ and the order with respect to RH is 0.8, while in polystyrene having $\bar{M}_n = 10^4$ the order with respect to PH is 0.6.[18]

Convincing evidence that in solution chain oxidation develops within a single macromolecule is provided by a comparison[14] of the rates of initiated oxidation of the n-decane–2,2,4-trimethylpentane and polyethylene–polypropylene systems. In the former case the rate of oxidation passes first through a maximum and then through a minimum with change in composition of the hydrocarbon mixture, such variation being due to the different activities of secondary and tertiary peroxy-radicals in chain propagation and termination[19]. In the latter case the rate of oxidation varies linearly with the composition of the polymer mixture, which indicates the absence of cross propagation and termination, possible only when the chain oxidation develops inside each separate coiled molecule.

Thus the kinetics of the oxidation of polymers in solution differs significantly from that of the oxidation of hydrocarbons in the participation of simple initiator or solvent radicals in chain termination, while chain oxidation develops within each macromolecule. Both circumstances result in slower oxidation of a polymer than of the model hydrocarbon.

III. REACTIVITY OF POLYMERS AND MODEL HYDROCARBONS

Since polymers and hydrocarbons differ in the kinetics of their initiated oxidation (Table 1), comparison of their rates of oxidation under similar conditions will not give a correct idea of the reactivities of carbon–hydrogen bonds in polymers and in model hydrocarbons. An example is provided by data on the oxidation of polypropylene and 2,2,4-trimethylpentane (RH) in the presence of 0.01 M azocyclohexanecarbonitrile in chlorobenzene at 363 K:[20] for the hydrocarbon the ratio $W_{O_2}/[RH]W_i^{1/2} = 4.1 \times 10^{-5}$ $M^{-1/2}$ $s^{-1/2}$, whereas the corresponding ratio for the polymer (per gram-equivalent of the monomer unit) is some hundredfold greater, i.e. 1.5×10^{-3}. We shall see below that the reactivity of a tertiary carbon–hydrogen bond in polypropylene is closely similar to that for 2,2,4-trimethylpentane.

During recent years rate constants have been measured for the reactions of peroxy- and alkoxy-radicals with carbon–hydrogen bonds in polymers and in model hydrocarbons. Cumene (RH) and polyethylene (PH) were oxidised together, and the quantities of ROOH and POOH were determined[21]. The ratio [POOH]/[ROOH] gave the ratio of the rate constants k_2^{PH}/k_2^{RH}, and k_2 was calculated for the reaction of the cumenylperoxy-radical with a carbon–hydrogen bond in polyethylene in solution. The rate of oxidation of polypropylene was measured in the presence of an initiator and t-butyl hydroperoxide[20], reaction with which caused rapid exchange of $PO_2^{\cdot}$ by $(CH_3)_3COO^{\cdot}$ radicals, so that the rate of oxidation of polypropylene was

$$W_{O_2} = (k_2/\sqrt{k_6}) \cdot [PH] \cdot [(CH_3)_3COO^{\cdot}]$$

from which k_2 could be calculated when k_6 was known. Peroxy-radicals of polystyrene (ps) recombine rapidly, so that its addition to cumene tended to inhibit oxidation of the latter[22]. The ratio k_2^{ps}/k_2^{RH} was found from the dependence of W_{O_2} on the concentration of polystyrene, and hence k_2^{ps} was calculated[22]. Rate constants for the abstraction of hydrogen from PH and RH by t-butoxy-radicals were measured by a method of competing reactions[23]. The results of these investigations are summarised in Table 2.

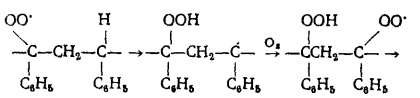
A comparison of polyethylene and polypropylene with model hydrocarbons shows that carbon–hydrogen bonds in a polymer and in the corresponding model have similar reactivities (differing not more than twofold, within the limits of error in the calculation of absolute rate constants). However, a marked (tenfold) difference in reactivity is observed between polystyrene and the model hydrocarbon cumene[22,25]. The most probable reason why a carbon–hydrogen bond is attacked more slowly in polystyrene when in cumene is steric hindrance by neighbouring phenyl rings. Detachment of hydrogen from such a

Table 2. Rate constants k* for reactions of peroxy- and alkoxy-radicals with C–H bonds in polymers and model hydrocarbons.

Oxidisable compound	Radical	Solvent	T, K	k, M^{-1} s^{-1}	Ref.
Polyethylene	$C_6H_5C(CH_3)_2OO^{\cdot}$	$C_6H_5CH(CH_3)_2$	388	0,12	21
n-Decane	$C_6H_5C(CH_3)_2OO^{\cdot}$	C_6H_5Cl	388	$10^{8,68}\exp(-73/RT)=0,063$	4
Polypropylene	$(CH_3)_3COO^{\cdot}$	C_6H_5Cl	363	0,98	20
2,6,10,14-Tetramethylpentadecane	$(CH_3)_3COO^{\cdot}$	C_6H_5Cl	363	0,58	20
Isopentane	$(CH_3)_2(C_2H_5)COO^{\cdot}$	$(CH_3)_2CHC_2H_5$	363	$10^{8,3}\exp(-66/RT)=0,35$	24
Polypropylene	$C_{10}H_{11}OO^{\cdot}$	C_6H_5Cl	363	3,3	20
2,6,10,14-Tetramethylpentadecane	$C_{10}H_{11}OO^{\cdot}$	C_6H_5Cl	363	2,1	20
Polystyrene	$C_6H_5C(CH_3)_2OO^{\cdot}$	$C_6H_5CH(CH_3)_2$	353	$10^{9,7}\exp(-72/RT)=0,10$	22
Cumene	$C_6H_5C(CH_3)_2OO^{\cdot}$	$C_6H_5CH(CH_3)_2$	353	$10^{6,7}\exp(-41/RT)=4,2$	25
Polystyrene	$(CH_3)_3CO^{\cdot}$	C_6H_6	313	26*	23
2,4-Dimethylpentane	$(CH_3)_3CO^{\cdot}$	C_6H_6	313	125*	23
Cumene	$(CH_3)_3CO^{\cdot}$	C_6H_6	313	1020*	23
Polystyrene	$(CH_3)_3CO^{\cdot}$	C_6H_6	318	26*	26
Cumene	$(CH_3)_3CO^{\cdot}$	C_6H_6	318	1600*	26
Polypropylene	$(CH_3)_3CO^{\cdot}$	C_6H_6	318	137*	26
2,2,4-Trimethylpentane	$(CH_3)_3CO^{\cdot}$	C_6H_6	318	300*	26

*Values of k calculated from k/k_d ratios, where $k_d = 10^{13.5}\exp(-69/RT)$ s^{-1} is the decomposition rate constant of the t-butoxy-radical (it has the values 100 and 140 s^{-1} at 313 and 318 K respectively)[27].

bond in cumene produces a cumenyl radical, which is stabilised by interaction of the p orbital of the unpaired electron with π orbitals of the phenyl ring. In polystyrene such stabilisation, which requires coplanarity of the phenyl ring and adjacent carbon–carbon bonds, is made difficult by neighbouring phenyl rings, which prevent such coplanarity. This explanation is supported by a comparison of the rate constants for reactions of the t-butoxy-radical with cumene, 2,4-diphenylpentane, and polystyrene (Table 2): rates of attack on a carbon–hydrogen bond are 5 times as rapid in diphenylpentane as in polystyrene, and ~10 times as rapid in cumene as in diphenylpentane. It is also interesting that the rate constant for chain propagation in polystyrene is $10^6 \exp(-33/RT) = 12.5\ M^{-1}\ s^{-1}$, which is hundredfold the rate constant for reaction of the cumenylperoxy-radical with a carbon–hydrogen bond in polystyrene [13]. If no experimental error is involved in the measurement of k_6 (which together with the ratio $k_2/k_6^{1/2}$ was used to calculate k_2), this can be explained by intramolecular chain propagation:



Thus carbon–hydrogen bonds in a polymer exhibit the same reactivity towards free radicals as do those in a model hydrocarbon, provided that neighbouring groups do not create steric hindrance, as occurs in polystyrene.

IV. SIMILARITY OF THE MECHANISMS OF OXIDATION OF LIQUID HYDROCARBONS AND SOLID POLYMERS

Solid carbon-chain polymers, like liquid hydrocarbons, are oxidised by a chain mechanism involving alkyl and peroxy-radicals. This is demonstrated by investigations on the initiated oxidation of polymers, in which $W_{O_2} \gg W_i$ at not very high rates of initiation, and the chain length usually varies over the range $\nu = 5-200$ monomer units.

Rate constants for initiation and for the decomposition of several initiators in polymers are given in Table 3. The liquid-phase chain oxidation of hydrocarbons involves alkyl and peroxy-radicals, the latter recorded by electron spin resonance [3]. The oxidation of solid polymers also is accompanied by formation of peroxy-radicals, detected by e.s.r. both in low-temperature radiation-chemical oxidation [43] and in oxidation in the presence of initiators at ~373 K (see Section VI).

During recent years important data on the mechanism of the oxidation of solid carbon-chain polymers have been obtained by the use of initiated oxidation, in which a known fixed rate of generation of free radicals enables the dependence of rate of oxidation on reactant concentrations and on rate of generation to be examined, the length of the chain to be calculated, and a quantitative measure of the oxidisability of a substance to be obtained as the overall constant in the formula

$$W_{O_2} = \text{const}\,[RH]^{n_1} \cdot [O_2]^{n_2} \cdot W_i^{n_3} \quad .$$

The rate of the initiated oxidation of solid polymers, like the liquid-phase oxidation of hydrocarbons, is proportional to $W_i^{1/2}$ (Table 4). Hence in both solid and liquid phases chain termination results from the encounter and loss of two active centres (bimolecularly). As in the liquid phase, the rate of oxidation is independent of the partial pressure of oxygen when the latter is "high" (~1 atm). [38]

It is interesting to compare the rates of oxidation of polymers and model hydrocarbons. For polyethylene the ratio $W_{O_2}/W_i^{1/2} = 0.9 \times 10^{-5}$ per methylene group at 373 K (Table 4 [40]); but for a methylene group in cyclohexane [44] $k_2 k_6^{-1/2} = 7.6 \times 10^{-5}$, an almost tenfold difference. On the other hand, polypropylene and isopentane are closely similar in oxidisability: $W_{O_2}/W_i^{1/2} = 6.4 \times 10^{-4}$ for one monomeric group in the polymer (Table 4 [38]) and $k_2 k_6^{-1/2} = 4.5 \times 10^{-4}$ for isopentane (373 K). [24] The fact that, in the absence of an inhibitor, the rate of oxidation of a polymer in the solid phase is directly proportional to $W_i^{1/2}$ proves that chain termination always occurs by a bimolecular

Table 3. Decomposition rate constants and efficiency of initiators in solid polymers ($k_i = 2ek$).

Initiator	Polymer	T, K	k or k_i, s^{-1}	e	Ref.
AIBN	polystyrene	353	—	0.05	28
AIBN	polystyrene	333—353	$k_i = 5.5 \cdot 10^{13} \exp(-128/RT)$	—	29
AIBN	polyethylene	335	$k_i = 0.8 \cdot 10^{-7}$	0.005	30
AIBN	polyethylene	343	$k_i = 0.3 \cdot 10^{-6}$	0.006	30
AIBN	polyethylene	363	$k_i = 9.3 \cdot 10^{-6}$	0.02	30
AIBN	polyethylene	365.5	$k_i = 4.7 \cdot 10^{-5}$	0.07	30
AIBN	polypropylene	333—358	$k_i = 5.1 \cdot 10^{17} \exp(-154/RT)$	0.05*	31
Benzoyl peroxide	polystyrene	329—355	$k = 2.6 \cdot 10^{17} \exp(-150/RT)$	—	32
Benzoyl peroxide	polystyrene	355—371.5	$k = 6.7 \cdot 10^{13} \exp(-126/RT)$	—	32
Benzoyl peroxide	polyethylene	365	$k_i = 4.5 \cdot 10^{-5}$	—	34
Benzoyl peroxide	polypropylene	365	$k_i = 4.5 \cdot 10^{-5}$	—	34
Benzoyl peroxide	polypropylene	360	$k_i = 5.9 \cdot 10^{-5}$	—	33
Benzoyl peroxide	polypropylene	344—365	$k = 8.4 \cdot 10^{13} \exp(-124/RT)$	0.14—0.62	35
Benzoyl peroxide	polypropylene	340—360	$k = 4.5 \cdot 10^{13} \exp(-124/RT)$	—	36
Benzoyl peroxide	polybut-1-ene	349—383	$k = 8.4 \cdot 10^{13} \exp(-124/RT)$	0.018—0.59	35
Benzoyl peroxide	poly-4-methylpent-1-ene	344—365	$k = 7.0 \cdot 10^{13} \exp(-122/RT)$	0.012—0.05	35
Benzoyl peroxide	poly(ethyl acrylate)	358—383	$k = 8.0 \cdot 10^{13} \exp(-123/RT)$	—	37
Benzoyl peroxide	poly(vinyl chloride)	337—350	$k = 1.55 \cdot 10^{20} \exp(-170/RT)$	—	32
Benzoyl peroxide	poly(vinyl chloride)	350—363	$k = 6.9 \cdot 10^{15} \exp(-162/RT)$	—	32
Benzoyl peroxide	poly(vinyl chloride)	363—371.5	$k = 1.2 \cdot 10^{15} \exp(-136/RT)$	—	32
Cumenyl peroxide	polyethylene	382—391	$k_i = 8.5 \cdot 10^{16} \exp(-157/RT)$	—	38
Cumenyl peroxide	polypropylene	373—395	$k_i = 1.1 \cdot 10^{13} \exp(-135/RT)$	—	34
Cumenyl peroxide	polypropylene	388	$k_i = 8.1 \cdot 10^{-6}$	—	33
Di-t-butyl peroxalate	polypropylene	298	—	0.014	39
Di-t-butyl peroxalate	polypropylene	308	—	0.033	39
Di-t-butyl peroxalate	polypropylene	318	—	0.061	39
Di-t-butyl peroxalate	polypropylene	328	—	0.15	39
Peroxide of plamitic acid	polystyrene	333—353	$k_i = 2.1 \cdot 10^{14} \exp(-127/RT)$	—	29
Peroxide of lauric acid	polystyrene	353	—	0.33	28
Peroxide of lauric acid	polyethylene	353	—	0.46	28

*At 353 K.

reaction. Therefore all schemes of uninhibited oxidation involving any linear mechanism of chain termination in the polymer[9,45-47] should be reconsidered as inconsistent with experiment.

Table 4. Values of $W_{O_2}/W_i^{1/2}$ for polymers in the solid phase.

Polymer	Initiator	T, K	$W_{O_2} W_i^{-1/2}$, mole$^{1/2}$ kg$^{-1/2}$ s$^{-1/2}$	Ref.
Polyethylene*	cumenyl peroxide	389—402	$1.6\cdot10^{10}\exp(-88/RT)$	40
Polyethylene*	$\gamma(^{60}Co)$	318	$1.25\cdot10^{-3}$	42
Polypropylene, isotactic*	benzoyl peroxide	353—378	$1.4\cdot10^{6}\exp(-56/RT)$	38
Polypropylene, atactic	$\gamma(^{60}Co)$	295	$4.0\cdot10^{-3}$	41
Polypropylene, atactic	$\gamma(^{60}Co)$	318	$1.2\cdot10^{-2}$	41
Polypropylene, isotactic*	benzoyl peroxide	344—378	$73\exp(-26/RT)$	35
Polypropylene, amorphous	benzoyl peroxide	358—378	$8.5\cdot10^{8}\exp(-71/RT)$	37
Polypropylene, isotactic*	azoisobutyronitrile, POOH	317—365	$4.0\cdot10^{2}\exp(-27.8/RT)$	31
Polybut-1-ene	benzoyl peroxide	363	$2.1\cdot10^{-2}$	35
Polybut-1-ene	benzoyl peroxide	378	$5.4\cdot10^{-2}$	35
Copolymer*, 37**	$\gamma(^{60}Co)$	318	$5.7\cdot10^{-3}$	42
Copolymer*, 73**	$\gamma(^{60}Co)$	318	$1.6\cdot10^{-3}$	42
Copolymer, 65**	benzoyl peroxide	358—378	$3.8\cdot10^{8}\exp(-71/RT)$	37
Copolymer, 87**	benzoyl peroxide	353—369	$2.7\cdot10^{6}\exp(-54/RT)$	38
Copolymer, 96**	cumenyl peroxide	388,5	$1.6\cdot10^{-2}$	38
Copolymer, 98**	cumenyl peroxide	382—400	$1.0\cdot10^{9}\exp(-81/RT)$	38
Poly(ethyl acrylate)	benzoyl peroxide	358—378	$7.6\cdot10^{5}\exp(-54/RT)$	37

*Calculated for the amorphous phase: i.e. multiplied by $\alpha^{1/2}$, where α is the fraction of the amorphous phase.
** Percentages of ethylene in its copolymers with propene.

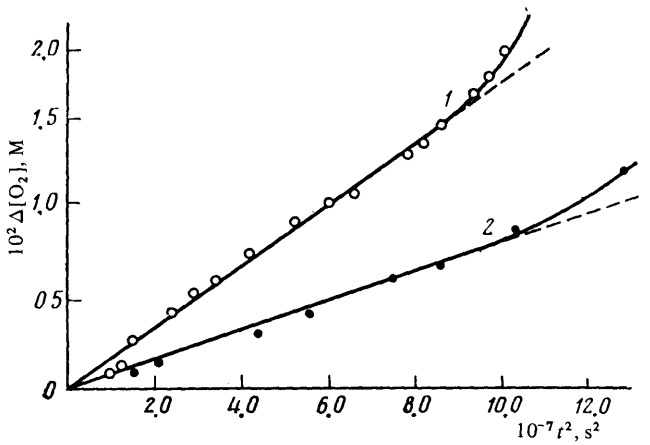


Figure 1. Kinetic curves for the autoxidation of polypropylene at 387 K under different oxygen pressures: 1) 1 atm; 2) 0.6 atm.

The uninitiated oxidation (autoxidation) of hydrocarbons and polymers is characterised by autocatalysis[3,7,48] due to the accumulation of hydroperoxide, an intermediate product that breaks down into free radicals. Both in liquid and in solid phases, therefore, oxidation is a self-initiated chain reaction (a chain reaction with degenerate branching of the chains). Since chains are terminated by a bimolecular reaction, the rate of autoxidation of a hydrocarbon is described by the equation[4]

$$d\Delta[O_2]/dt \cong k_2 k_6^{-1/2}\cdot[RH]\cdot(k_3[ROOH])^{1/2}$$

or

$$\Delta[O_2] \cong \frac{1}{4}(k_2 k_3^{1/2} k_6^{-1/2}\cdot[RH])^2\cdot t^2$$

provided that the rate of generation of chains is small ($W_{i0} \ll k_3[ROOH]$ almost throughout the experiment) and the whole of the oxygen absorbed is converted into hydroperoxide. The parabolic kinetic law, $\Delta[O_2] \propto t^2$ is due to the fact that self-initiation is a first-order reaction, whereas chain termination has a bimolecular mechanism. Both factors apply also to the oxidation of polymers in the solid phase, which therefore is also described (Fig. 1) by the kinetic law

$$\Delta[O_2]^{1/2} = b\cdot t\ .$$

In view of the above considerations use of the kinetic law $\Delta[O_2] \propto e^{\varphi t}$ (e.g. Ref. 48) for the uninhibited oxidation of solid polymers is evidently incorrect.

Thus oxidation both of liquid hydrocarbons and of solid carbon-chain polymers is a self-initiated chain reaction involving alkyl and peroxy-radicals with bimolecular chain termination. Within the framework of such a definition we can speak of a single radical–chain mechanism for the oxidation of liquid hydrocarbons and solid polymers. It is interesting that the gas-phase oxidation of hydrocarbons falls outside the scope of such a definition and has a different mechanism[49], in which not only R$^\cdot$ and RO$_2^\cdot$ but also alkoxy-radicals play an important part in chain propagation, and the reaction between two RO$_2^\cdot$ radicals involves not termination but propagation: $2RO_2^\cdot \rightarrow 2RO^\cdot + O_2$.

V. PRIMARY RADICAL REACTION IN A POLYMER MATRIX

In a condensed phase (liquid or solid) a bimolecular reaction between freely diffusing reactants takes place in two stages, with diffusion of two particles into the same cage followed by their collision and reaction in the cage[50]:

$$A + B \underset{k_D}{\overset{k_D}{\rightleftarrows}} A\cdot B \xrightarrow{k} \text{Products}\ .$$

Depending on the relation between k and k'_D reactions are divided into slow ($k \ll k'_D$) and rapid or diffusion-controlled ($k \geqslant k'_D$). In a solution the cage walls consist of molecules undergoing quite rapid rotation (10^9-10^{11} s^{-1}) and translation (a molecular diameter in $10^{-9}-10^{-10}$ s). In the liquid phase, therefore, the form of the cage changes rapidly, and in the absence of orientational interactions between the molecules the cage walls can be regarded as an isotropic viscous medium surrounding the pair of reacting particles. In such a cage it may be expected that all mutual orientations of the particles will be equivalent, and that the steric factor for the bimolecular reaction will be closely similar to that for a gas-phase reaction.

An amorphous polymer phase resembles a liquid with regard to molecular motion, but displacements and rotations of segments and molecules are comparatively slow owing to the great length of the macromolecular chains and the large energy of intermolecular interaction of the chains. As a consequence, the shape of the cage formed by segments of the macromolecule changes slowly in the amorphous phase when compared with the liquid, the relaxation time of the form of the cage in the polymer is long, and the cage can be regarded as a kind of "bag" with rigid walls surrounding the pair of reactant particles[51]. In such a "rigid" cage by no means all the mutual orientations of the reactant particles are energetically equivalent. If an

orientation required the consumption of energy is necessary for a primary step, the steric factor P for such a reaction will be smaller in the polymer than in the liquid phase, and will depend on the temperature: $P = P_0 e^{-E_{or}/RT}$, where E_{or} is the activation energy of orientation of the particles due to the energy consumed in overcoming the action of the rigid polymer matrix, i.e. in orienting the particles. Such a model of a rigid cage (a cage with slow relaxation of its shape and size) leads to the qualitative conclusions outlined below[51].

1. The rate constant for species requires a precise orientation before they can react should be smaller in a solid polymer matrix than in the liquid phase. This conclusion is supported by comparison of the rate of such reactions as the oxidation of dinaphthyl-*p*-phenylenediamine by a hydroperoxide ($k_*/k_{sd} = 7.4$ in polypropylene at 373 K [52]), the reaction of tri-t-butylphenoxyl with POOH (43 in polypropylene at 295 K [53]), and the action of the nitroxyl radical on 2,6-di-t-butylphenol[54] (14 in polyethylene at 313 K).

2. The activation energy of a bimolecular reaction should be greater in the solid phase than in solution. This conclusion is consistent with data on termination reactions: for the reaction of 2,4,6-tri-t-butylphenoxyl with POOH in benzene and in polypropylene the activation energy is respectively 45.5 and 67 kJ mole^{-1};[53] the corresponding values for the action of the nitroxyl radical on 2,6-di-t-butylphenol are 42 and 75 kJ mole^{-1}.[54]

3. Introduction of a simple compound into a polymer, by increasing the molecular mobility and making the cage more elastic (shortening the relaxation time of its shape), should accelerate a bimolecular reaction. Benzene actually has such an effect on the above two reactions[53,54].

4. Since both the mutual orientation of species and the rotation of a species in a cage involve overcoming forces of repulsion due to "neighbours", a parallelism can be expected in the variation of the rate constant of a bimolecular reaction and the frequency of rotation of a species, e.g. a stable nitroxyl radical, with change in the polymer matrix. Such parallelism has been demonstrated[12,53,54]. It is interesting that the activation energy of rotation E_ν and the difference in activation energy of the reaction in solid and liquid phases are then closely similar (respectively 40 and 33 kJ mole^{-1}).[53,54]

5. Rise in temperature is accompanied by an increase in molecular mobility in the polymer, a shortening of the relaxation time of the cage shape, and an increase in the elasticity of the cage. As a consequence, the orientation of the reactant species necessary for the primary step is more easily attained, and E_{or} is lowered. Thus, since in the solid phase the total activation energy $E_\Sigma = E_{or} + E$, while E_{or} decreases with rise in temperature, it follows that E_Σ is an effective quantity that decreases with rise in temperature.

Termination in the solid phase may also be retarded by a possible delay between the abstraction of hydrogen and rehybridisation of p orbitals of the carbon atom under attack[55]. However, the difference between the rate constants for abstraction of a hydrogen atom by peroxyradicals in solution and in the solid phase (see below) is small, so that delay in rehybridisation is not evident here. At the given temperatures the molecular mobility of the macromolecular segments is apparently sufficient to ensure rehybridisation of orbitals immediately on accomplishment of the primary step.

Another substantial difference between a solid polymer and a liquid is the inhomogeneity of a polymer as a medium. Firstly, a polymer (polyethylene, isotactic polypropylene, ethylene–propylene copolymers, etc.) comprises crystalline and amorphous phases. If the former is more densely packed than the latter, dissolution and interaction of the reactants will occur predominantly in the amorphous phase. Electron spin resonance has shown[53] that nitroxyl radicals dissolve only in the amorphous phase. Secondly, the amorphous phase of a polymer is itself non-uniform, consisting of a series of zones differing in molecular mobility. This leads to so called polychromatic kinetics both of radical reactions and of physical processes, e.g. diffusion in a polymer[56–60]. With rise in temperature the polychromatism disappears, apparently because of increasing mobility of the molecules and more rapid migration of density fluctuations along the polymer (the amorphous phase approaches a liquid in molecular mobility). Thus a polymer differs from a liquid as a medium in its more rigid cage structure (the shape of the cage changes slowly) and in inhomogeneity. These two features affect the kinetics of radical reactions in a polymer.

Table 5. Specific rates of generation of chains in polymers and model hydrocarbons.

Oxidisable compound	T, K	k_{i0}, M^{-1} s^{-1}	E_{i0}, kJ mole^{-1}	Ref.
Polypropylene (solid)*	405	$8.5 \cdot 10^{-5}$	92	63
Polypropylene (solution)	403	$2.9 \cdot 10^{-6}$	98	63
Isopentane	410	$1.3 \cdot 10^{-8}$	158	64
Low-pressure polyethylene* (solid)	404	$1.3 \cdot 10^{-5}$	117	63
High-pressure polyethylene* (solid)	377	$2.5 \cdot 10^{-6}$	146	63
n-Heptane	406	$2.3 \cdot 10^{-9}$	181	65

*Here calculation of k_{i0} per monomer unit was based on the amorphous phase.

VI. CHAIN GENERATION AND PROPAGATION

Generation of Chains

In hydrocarbons undergoing oxidation, chains are generated by reactions involving oxygen. Most often generation occurs by the bimolecular reaction[61]

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot},$$

whose activation energy approximates to its endothermicity. In compounds having weak carbon–hydrogen bonds (bonding energy < 330 kJ mole^{-1}) chains are generated mainly by the termolecular reaction[3]

$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2 .$$

The reaction

$$C_6H_5CH_2CH_3 + 2O_2 \rightarrow C_6H_5\dot{C}HCH_2 + 2HO_2^{\cdot}$$

has been demonstrated[62] for ethylbenzene.

In the only study of chain generation in polymers (polyethylene, polypropylene)[63] the rate of formation of radicals was measured by an inhibitor method from the consumption of 1-naphthol and *NN'*-dinaphth-2-yl-*p*-phenylenediamine. Chain generation was shown to involve

oxygen, which in effect dissolves only in the amorphous phase, so that generation was concentrated therein. In the solid phase the specific rate of chain generation $k_{i0} = W_{i0}/\alpha[O_2][PH]$ (in which α is the fraction of the amorphous phase) is significantly higher than in solution (Table 4) and higher than in model hydrocarbons by several orders of magnitude. In a polymer chains are probably generated by reaction between oxygen and residues of the catalyst. The higher specific rate in the solid phase than in solution (Table 5) can be explained by the presence of "weak" carbon–hydrogen bonds in deformed segments of the macromolecular chains. A relatively high rate in polymers must be taken into account in the use of inhibitors for the stabilisation of polymers and in interpretation of the results of experiments with inhibitors. In particular, the high value of W_{i0} in polypropylene casts doubt on the legitimacy of applying the theory of critical phenomena in inhibited oxidation, since quite a high k_3/W_{i0} ratio is then necessary [66].

Reaction $P^{\cdot} + O_2 \rightarrow PO_2^{\cdot}$

The addition of oxygen to alkyl radicals is very rapid, its rate being limited by diffusion of the gas into the polymer. For example, the rate constant for addition of oxygen to the methyl radical in water is 5×10^9 M^{-1} s^{-1}. [19] The kinetics of the $P^{\cdot} + O_2$ reaction in polymers has been studied by low-temperature e.s.r. with radiation-chemical generation of $P^{\cdot}$ (Table 6). Owing to the non-uniformity of the polymer and differences in the diffusion coefficients of oxygen in different zones, the reaction with alkyl radicals is described by a polychromatic kinetic equation with an activation-energy particle distribution (every zone has its own activation energy for the diffusion of oxygen). Table 6 gives values of Emin and Emax calculated for a linear energy distribution of $P^{\cdot}$. Earlier measurements of k_1 and E_1 have been given in a review [5].

Table 6. Rate constants of the reaction $P^{\cdot} + O_2$ in polymers.

Polymer	T, K	E, kJ mole^{-1}	lg(A, M^{-1} s^{-1})	Ref.
Isotactic polypropylene, powder	373	—	6.4*	34
Isotactic polypropylene, film	100—140	E_{min}=33; E_{max}=44	14	67
Atactic polypropylene, film	100—140	E_{min}=19; E_{max}=25	9	67
Polystyrene	90—120	E_{min}=29; E_{max}=35	13	68
Polystyrene	94—140	E_{min}=22.5; E_{max}=27	12	69

*Value of lg(k, M^{-1} s^{-1}).

Since diffusion in a polymer is due to segmental mobility, while rise in temperature produces an abrupt release of degrees of freedom, it follows that $E_{diff} = E_1$ changes from one temperature range to another. Therefore the extrapolation of k_1 to the comparatively high oxidation temperatures will give incorrect estimates. The only estimate of k_1 for 373 K (oxidation temperature) was based [34] on the dependence of rate of oxidation on partial pressure of oxygen (the ratio $k_1/k_4^{1/2}$ was found) with the value $k_4 = 2.7 \times 10^6$ M^{-1} s^{-1} measured by e.s.r.

The Reaction $PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot}$

Reaction rate constants for peroxy-radicals in polymers have been studied by electron spin resonance—at low temperatures (below room temperature) from the kinetics of the disappearance of $PO_2^{\cdot}$, and under oxidation conditions from the rate of oxidation at the steady-state concentration of peroxy-radicals ($k_2 = W_{O_2}/[PO_2^{\cdot}]$)—and the results are listed in Table 7. The activation energy for the $PO^{\cdot} + PH$ in polyethylene [70] seems to be greatly underestimated. It must be expected that in the solid phase $E > E_{liq}$. For the reaction of cumenylperoxy-radicals with n-decane $E_2 = 73$ kJ mole^{-1} (Table 2), whereas in polyethylene $E_2 = 39$ kJ mole^{-1} (Table 7). Furthermore, a carbon–hydrogen bond in polyethylene is more stable than a tertiary bond in polypropylene, so that E_2 should be higher in the former than in the latter polymer, whereas the opposite situation has been observed [70]. On the other hand, E_2 is higher in deuterated than in ordinary polyethylene, which indicates the loss of $PO_2^{\cdot}$ by reaction with a C–H (C–D) bond.

Table 7. Rate constants of $PO_2^{\cdot} + PH$ reactions in solid polymers calculated per monomer unit.

Polymer	Initiation	T, K	A, M^{-1} s^{-1}	E, kJ mole^{-1}	Ref.
Polyethylene	γ (Co^{60})	230—270	$8.4 \cdot 10^2$	39	70
Deuterated polyethylene	γ (Co^{60})	270—300	$9.6 \cdot 10^2$	43	70
Isotactic polypropylene	POOH	383—413	$3.0 \cdot 10^5$	38	71
Isotactic polypropylene	AIBN, POOH	317—365	$9.6 \cdot 10^{11}$	87.8	31
Amorphous polypropylene	benzoyl peroxide	363—378	$1.6 \cdot 10^7$	51	35
Amorphous polypropylene	di-t-butyl peroxolate	318	$7.7 \cdot 10^{-3}$***		42
Isotactic polypropylene	γ (Co^{60})	270—310	$1.1 \cdot 10^4$	53	70
Isotactic deuterate polypropylene	γ (Co^{60})	270—310	$1.5 \cdot 10^4$	58	70
Amorphous polystyrene	mechanochemical	210—293	$3.5 \cdot 10^8$**	43*	72
Amorphous polystyrene	mechanochemical	210—293	$1.3 \cdot 10^{12}$***	88**	72
Poly(methyl methacrylate)	mechanochemical	250—360	$1.0 \cdot 10^6$	50	73

*For maximum value of k_2.
**For minimum value of k_2.
***Value of k.

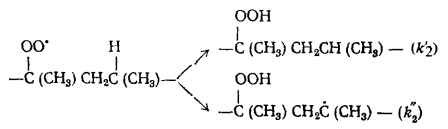
Values of k_2 must be expected to be smaller in the solid phase than in solution (see above and Tables 2 and 7). In solution at 388 K the cumenylperoxy-radical attacks a carbon–hydrogen bond in polyethylene with $k_2 = 0.12$ M^{-1} s^{-1}. In the solid phase extrapolation of k_2 to 388 K gives 0.0012 M^{-1} s^{-1} per bond (Table 7): i.e. in the solid phase abstraction of a hydrogen atom by the peroxy-radical is slower by a factor of 100.

We reach a similar conclusion if we compare $k_2 = 0.05$ M^{-1} s^{-1} in poly(methyl methacrylate) [monomeric unit $-CH_2\overset{|}{C}(CH_3)COOCH_3$] at 360 K with the rate constant $k_2 = 24$ M^{-1} s^{-1} for reaction of the cumenylperoxy-radical with methyl propionate at the same temperature [4]. At first glance a different conclusion is reached from a comparison of k_2 for polypropylene in solution and in the solid phase: the t-butylperoxy-radical attacks a tertiary carbon–hydrogen bond in polypropylene with $k_2 = 0.98$ M^{-1} s^{-1} at 338 K (Table 2), whereas in solid atactic polypropylene $k_2 = 0.7$ M^{-1} s^{-1} (Table 7). [35] However, these constants represent different processes. In the oxidation of polypropylene in the presence of a hydroperoxide in solution k_2 relates to

the reaction

$$(CH_3)_3COO^{\cdot} + PH \rightarrow (CH_3)_3COOH + P^{\cdot}\ .$$

Chain propagation in such oxidation in the solid, like the oxidation of hydrocarbons with neighbouring tertiary carbon–hydrogen bonds in the β position[3], occurs by intermolecular and intramolecular mechanisms:



For oxidation in the solid phase, therefore, $k_2 = k_2' + k_2''/[PH]$. For 2,4-dimethylpentane $k_2''/k_2' = 90$ at 373 K if k_2' relates to a single tertiary carbon–hydrogen bond[74]. Assuming the same relation for polypropylene, with the use of $k_2 = 0.7$ and $[PH] = 22$ M, we obtain $k_2' = 0.18$ $M^{-1}\ s^{-1}$, about one-fifth of the value in the liquid phase.

Thus reaction of a peroxy-radical with a carbon–hydrogen bond takes place more slowly in a solid polymer than in the liquid phase. This is due to the effect of the rigid cage of the polymer matrix on the probability of achieving the mutual orientation of radical and bond required for the reaction. This is consistent also with the polychromatic reaction kinetics of peroxy-radicals in polystyrene[72], which cannot be explained by hindrance to translational or rotational diffusion of segments, since in this case we are dealing with a slow reaction not controlled by such diffusion of species.

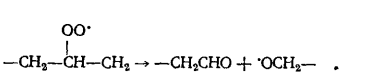
Breakdown of Macroradicals

The oxidation of polymers is accompanied by degradation of the macromolecules and a fall in the molecular mass of the polymer. The mechanism of this process still remains obscure. Since alkoxy-radicals tend to break down, but are formed by the decomposition of hydroperoxides, it was natural to attribute degradation of the macromolecules to breakdown of POOH:[48]

$$POOH \rightarrow HO^{\cdot} + PO^{\cdot} \rightarrow \text{decomposition.}$$

However, experiments on the initiated oxidation of polymers have shown that degradation begins with the appearance of peroxy-radicals long before a hydroperoxide has accumulated and begun to break down at an appreciable rate[37,75].

Tobolsky found[37] that the rate of degradation of polypropylene $W_S \propto W_i$ (with benzoyl peroxide as initiator at 363–378 K). Since in a steady state rate of initiation and of loss of radicals are equal, while tertiary peroxy-radicals also react to form alkoxy-radicals $2PO_2^{\cdot} \rightarrow 2PO^{\cdot} + O_2$, degradation was attributed to the generation of $PO^{\cdot}$ radicals and their subsequent decomposition. However, the relation $W_S \propto W_i^{1/2}$ is observed[75] in the oxidation of polyethylene (at 115 °C): i.e. W_S is directly proportional to the concentration of peroxy-radicals, and rupture of a carbon–carbon bond is a first-order reaction with respect to $PO_2^{\cdot}$. By analogy with the breakdown of $PO_2^{\cdot}$ in the gas phase[2] it is suggested[75] that such rupture is effected by the reaction

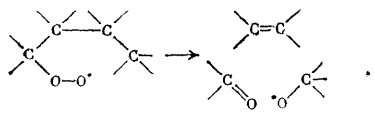


With the oxidation of methane as example, however, it has recently been convincingly demonstrated[49] that degradation in gas-phase oxidation has the mechanism

$$2RO_2^{\cdot} \rightarrow 2RO^{\cdot} \rightarrow \text{decomposition.}$$

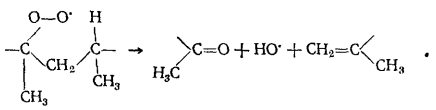
Hence there are no grounds for the first mechanism of degradation.

Marchal suggests[76] the mechanism



However, such intramolecular incorporation of oxygen of the peroxy-radical (radical substitution) is improbable, since the activation energy of this process followed by decomposition would be very high.

The most probable mechanism is breakdown of the peroxy-radical by degradative isomerisation:



VII. RELAY MECHANISM OF MIGRATION OF A FREE ELECTRON IN A POLYMER

In liquid free radicals ($R^{\cdot}$, $RO_2^{\cdot}$) migrate by diffusion, and chain termination either occurs with a diffusion rate constant ($R^{\cdot} + R^{\cdot}$, $R^{\cdot} + RO_2^{\cdot}$) or is determined by the rate of interaction of radicals ($RO_2^{\cdot} + RO_2^{\cdot}$). In a solid polymer a macroradical hardly diffuses at all[77], but segments of the macromolecule (macroradical) are displaced by thermal motion. In polymers undergoing oxidation, chains can in general be terminated by one of three mechanisms.

The first mechanism is segmental diffusion: a segment carrying the free electron, as it moves, encounters another segment, a radical, with which it interacts. Segmental diffusion provides a satisfactory explanation of the kinetics of the loss of alkyl macroradicals at low temperatures, and notably the "stepwise" character of their disappearance, which is due also to the non-uniformity of the polymer. Segmental diffusion is a slow process: e.g. in an ethylene–propylene copolymer (mol. wt. 200 000) $D = 4 \times 10^{-17}$ $cm^2\ s^{-1}$ at 220 K.[78] Displacement of a segment is restricted to an effective distance l. At the temperatures of oxidation (350–450 K) the loss of radicals is far more rapid than could be due to segmental diffusion, so that another hypothesis was required.

A second hypothetical mechanism of chain termination involved the formation of simple radicals, their rapid diffusion, and their recombination with macroradicals[79]. This hypothesis is open to several objections. Firstly, radicals of low molecular weight should appear at a rate exceeding the rate of initiation, but they can be formed only in the slow endothermic decomposition of radicals. On the assumption that termination is limited by the rate of such decomposition, it should be linear, whereas in oxidation termination is always bimolecular (Section IV). Secondly, if such active radicals as $HO^{\cdot}$ and $RO^{\cdot}$ are formed, they will react rapidly with carbon–hydrogen bonds in the polymer and, because of the low steady-state concentration, will be unable to participate in chain termination. For example, t-butoxy-radicals abstract hydrogen from tertiary carbon–hydrogen bonds in aliphatic hydrocarbons with $k = 80\,000$ $M^{-1}\ s^{-1}$ at 408 K,[19] and in polypropylene with a rate of formation $r_{O^{\cdot}} = 10^{-6}$ M s^{-1}

their steady-state concentration is $\sim 10^{-12}$ M; with $[P^{\cdot}] = 10^{-6}$ M and $k_D = 10^8$ M^{-1} s^{-1} we obtain $W_{P^{\cdot} + rO^{\cdot}} \simeq 10^{-10}$. Substantial difficulties arise when an attempt is made to write down specific decomposition reactions. A terminal alkyl radical usually breaks down to form a monomer and a macroradical [polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), etc.]; and a central alkyl macroradical mostly decomposes into a macromolecule and a macroradical. Therefore chain termination involving radicals of low molecular weight in hydrocarbon polymers undergoing oxidation is improbable in the absence of compounds of low molecular weight.

A mechanism of migration of a free electron in the form of simple radicals may develop when the polymer contains a highly active simple compound that reacts rapidly with the macroradicals. Introduction of cumenyl hydroperoxide, for example, retards the initiated oxidation of polypropylene and arrests the oxidation of polyethylene [80] by means of the reaction

$$PO_2^{\cdot} + rOOH \rightarrow POOH + rO_2^{\cdot}$$
$$rO_2^{\cdot} + PO_2^{\cdot} \rightarrow \text{Molecular products}.$$

Rapid diffusion of $rO_2^{\cdot}$ ensures comparatively rapid termination of chains. Simple compounds such as the lower aldehydes and hydroperoxides are formed in the later stages of the oxidation of polymers as a result of the degradation of POOH, and may also be involved in transmitting free electrons along the polymer [79]. However, such a mechanism of chain termination cannot develop in the early stages of oxidation of a high polymer unless special additives are present.

Table 8. Effective $PO_2^{\cdot}$ loss rate constants in solid polymers at $p_{O_2} = 1$ atm.

Polymer	T, K	k_6, M^{-1} s^{-1}	Ref.
Isotactic polypropylene	383	$4 \cdot 10^{5}$*	71
Amorphous polypropylene	363—378	$1.1 \cdot 10^{13}$ exp (—48.5/RT)	35
Isotactic polypropylene	328—363	$1.5 \cdot 10^{21}$ exp (—119/RT)**	82
Amorphous polypropylene	331—336	$5.0 \cdot 10^{10}$ exp (—52/RT)	42
Polystyrene	247—413	$6 \cdot 10^{13}$ exp (—75/RT)	84, 85
Polystyrene	265—283	10^{14} exp (—73,5/RT)	83
Poly(methyl methacrylate)	278—310	$6 \cdot 10$ exp (—75/RT)	84, 85
Poly(methyl methacrylate)	273—292	$3 \cdot 10^{12}$ exp (—71/RT)	86
Poly(methyl methacrylate)	293	0,36	87
Poly(vinyl acetate)	347—310	$6 \cdot 10^{12}$ exp (—75/RT)	84, 85

*Calculated from published data [71] by means of the formula $k_6 = W_i/[PO_2^{\cdot}]$, with $W_i = W_{O_2}^2/a^2$, in which $a = W_{O_2} W_i^{-1/2}$, taken from Ref. 38 (Table 4).

**Calculated for the amorphous phase.

A third possibility is that the free electron may migrate as a macroradical in the polymer by the so called relay mechanism [81]: the fragment of the macromolecule bearing the free electron moves by segmental diffusion, which is followed by chemical transfer of the electron to another segment, and so on, until two radicals meet and react. A relay mechanism of free-electron migration along a polymer during its oxidation is convincingly supported by the following facts. (i) The irradiation of polymers in the presence of oxygen yields free radicals, whose loss in the absence of an initiating effect is accompanied by the absorption of oxygen [43]. Several oxygen molecules are absorbed per $PO_2^{\cdot}$ radical lost: i.e. disappearance of the radicals is accompanied by the chain reaction

$$PO_2^{\cdot} \xrightarrow{PH} P^{\cdot} \xrightarrow{O_2} PO_2^{\cdot} \rightarrow \ldots,$$

and the encounter and loss of radicals result from their relay migration. (ii) Introduction of a chemically inert solvent into the polymer increases segmental mobility and also the average distance l through which the segment carrying the free electron moves during its lifetime. Thus the "relay distance" is increased and hence also the effective rate constant of recombination of the radicals. Addition of benzene to polypropylene and polystyrene produces a very considerable increase (by factors of 10—100) in the corresponding constant for bimolecular loss of $PO_2^{\cdot}$. [83] (iii) Since relay migration of the free electron involves a step of chain propagation, the inequalities $E_6^{PH} > E_6^{RH}$ and $E_6^{PH} > E_2^{PH}$ (the superscripts PH and RH denote media in which E_6 has been measured for peroxy-radicals of similar structure). This is consistent with experiment: values of 48 and 52 kJ $mole^{-1}$ have been obtained for E_6 in amorphous polypropylene, and 119 in the isotactic polymer (Table 8), while for cumenylperoxy-radicals in cumene $E_6 = 25$ kJ $mole^{-1}$, [19] so that $E_6^{PH} > E_6^{RH}$; since in isotactic polypropylene $E_2 = 88$ kJ $mole^{-1}$, we have $E_6^{PH} > E_2^{PH}$. (iv) The inhibiting effect of cumenyl hydroperoxide on the initiated oxidation of polyethylene and polypropylene [80] is also consistent with a relay mechanism, since inhibition can be explained by substitution of more rapid diffusion for the comparatively slow relay mechanism.

Table 9. Segmental movement (relay distance l) in the loss of free radicals in polymers.

Polymer	Valency-transfer reaction	T, K	$10^6 l$, cm	Δt, s	Ref.
Polyethylene	$P^{\cdot}$+PH	363	0.5	—	90
Polypropylene	$P^{\cdot}$+PH	373	1.7	0.015	34
Poly(methyl methacrylate)	$P^{\cdot}$+PH	311	0.55	—	90
Poly(methyl methacrylate)	$P^{\cdot}$+PH	328	0.15	—	90
Polyethylene	$PO_2^{\cdot}$+PH	363	0.35	—	90
Polypropylene	$PO_2^{\cdot}$+PH	292	0.75	—	90
Polypropylene	$PO_2^{\cdot}$+PH	323	0.37	—	89
Polypropylene	$PO_2^{\cdot}$+PH	383	2.4	0.12	71
Polypropylene	$PO_2^{\cdot}$+PH	383	1.7	0.21	82
Polypropylene	$PO_2^{\cdot}$+PH	383	4.7	0.14	35

Two parameters—the relay distance l and the specific rate of transfer of the free electron to another segment by chemical reaction—determine the effective rate constant with which two radicals meet. In the absence of oxygen transfer of the free electron takes place by the reaction

$$P^{\cdot} + PH \xrightarrow{k_1'} PH + P^{\cdot}.$$

The distance l can be estimated from experimental data in three ways.

Firstly, the bimolecular rate constant for the loss of radicals in the polymer can be used. In the amorphous phase of isotactic polypropylene, for example, $k_4 = 2.7 \times 10^6$ M^{-1} s^{-1} at 373 K.[34] With a relay mechanism $k_4 = 4 \times 10^{-3} \pi N l^3 k_i' [PH] \alpha_4$ M^{-1} s^{-1}, where N is Avogadro's number, l is expressed in centimetres, and α_4 is the probability of reaction between two P$^\cdot$ radicals $< 2l$ apart. On the assumption that the reaction P$^\cdot$ + PH takes place in PH with the same rate constant as the reaction $CH_3^\cdot + CH_4$ in the gas phase, where the rate constant is 3 M^{-1} s^{-1} at 373 K,[88] we find with [PH] = 22 M, $\alpha_4 = 1$, and $k_4 = 2.7 \times 10^6$ that $l = 17$ nm.

Secondly, the distance l can be identified with the radius of the "cage" in which two macroradicals meet as a consequence of segmental diffusion[78]. This radius can be estimated from experimental data on the kinetics of the loss of P$^\cdot$ in the polymer by means of the equation

$$l^{-1}([P^\cdot]^{-1} - [P^\cdot]_0^{-1}) = k_4(1 + 2\sqrt{\tau/t})$$

(where $\tau = l^2/\pi D$ and $k_4 = 4 \times 10^{-3} \pi N l D$, in which D (cm^2 s^{-1}) is the diffusion coefficient and values of l are given in Table 9), describing the kinetics of the diffusion loss of P$^\cdot$ and allowing for the initially non-stationary character of the process[78]. In the presence of oxygen the relay migration of a free electron is also a chain reaction accompanied by the absorption of oxygen. This is used to estimate l (cm) from the relation between the quantity of P$^\cdot$ that has disappeared and the oxygen absorbed[89] (Table 9):

$$\Delta[O_2] = l^{-3} \ln([P^\cdot]/[P^\cdot]_0)$$

where $\Delta[O_2]$ is expressed in mol.cm^{-3}.

When $[O_2]$ is sufficiently high and P$^\cdot$ radicals are converted rapidly into $PO_2^\cdot$, so that relay transfer is limited by the reaction $PO_2^\cdot$ + PH, we can estimate l also from the rate constants k_2 and k_6. In polypropylene chain propagation takes place both intra- and inter-molecularly at the respective rates $k_2''[PO_2^\cdot]$ and $k_2'[PH][PO_2^\cdot]$, but only the latter process is involved in the relay mechanism. By analogy with 2,4-dimethylpentane[74] we can put $k_2''/k_2' = 90$ at 373 K and $k_2' = 0.2k_2$, where k_2 is the overall propagation rate constant. Hence for polypropylene we obtain $k_6/k_2 = 8 \times 10^{-4} \pi N l^3 \alpha_6$, which enables l_{min} to be estimated with $\alpha_6 = 1$. Table 9 shows that segmental movements are quite large—of the order 10^{-7}–10^{-6} cm in 0.1–0.01 s—i.e. at a mean speed of 10^{-6}–10^{-4} cm s^{-1}, while $L_{segm} = 10^{-12}$–10^{-10} cm^2 s^{-1} at around 373 K. The comparatively high segmental mobility also ensures relatively rapid migration and meeting of free electrons during the oxidation of such polymers as polyethylene and polypropylene. Since a polymer is non-uniform, with zones differing in segmental mobility, polychromatic kinetics is observed in the recombination of radicals at low temperatures[56–59].

The relay mechanism of migration of the free electron explains also why oxidation of a solid polymer is local in character, i.e. why each chain develops and terminates within a small volume. Because of the comparatively short relay distance the displacement of the free electron during such development is around $l\nu^{1/2}$, where ν is the length of the chain; with $\nu = 30$ and $l = 10^{-6}$ cm this displacement is $\sim 5 \times 10^{-6}$ cm. Therefore a mixture of polymers, e.g. polyethylene and polypropylene, is oxidised additively[38]: $W_\Sigma = W_{pe}V_{pe} + W_{pp}V_{pp}$, where W_{pe} is the rate of the initiated oxidation of polyethylene, while V_{pe} is the fraction of polyethylene by volume. Under the same conditions the rate of oxidation of copolymers of ethylene and propylene varies non-additively with composition[38]:

$$W_\Sigma \neq W_{pe} \cdot [-CH_2-CH_2-] + W_{pp} \cdot [-CH_2CH(CH_3)-],$$

just as for a mixture of n-decane and iso-octane, because of the different activities of secondary and tertiary peroxyradicals in acts of chain propagation and termination.

VIII. REACTIONS OF ALKYL MACRORADICALS IN POLYMERS UNDERGOING OXIDATION

1. Diffusion and Kinetic Régimes of Oxidation

The oxidation of a polymer is preceded by the dissolution of oxygen in it. In a steady state, when the rates of oxidation and dissolution are equal, the process is described by the diffusion equation

$$d^2[O_2]/dx^2 = W_{O_2}/D,$$

where D is the diffusion coefficient for oxygen in the polymer and x the distance from the surface. Several studies have been made at low oxygen concentrations[91,92], when the rate of oxidation $W_{O_2} = \beta[O_2]$, where $\beta = k_1 k_4^{-1/2} W_i^{1/2}$. For a film $2l$ thick the depth x distribution of oxygen is given by

$$[O_2] = \gamma p_{O_2} \frac{\cosh[(l-x)\sqrt{\beta/D}]}{\cosh[l\sqrt{\beta/D}]},$$

in which γ is the Henry coefficient. The formula

$$\overline{[O_2]} = \gamma p_{O_2} l^{-1} (D/\beta)^{1/2} \tanh[l \cdot \sqrt{\beta/D}]$$

gives the average concentration of dissolved oxygen across the film.

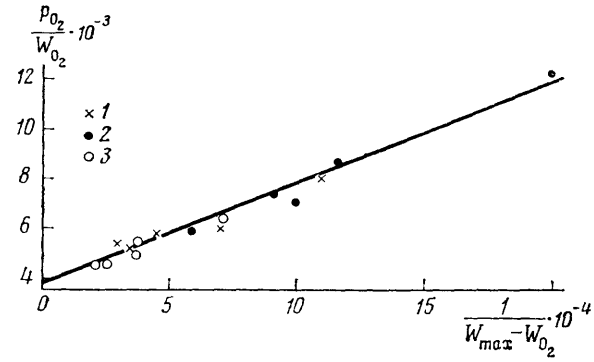


Figure 2. Dependence of p_{O_2}/W_{O_2} on $(W_{max} - W_{O_2})^{-1}$ for the oxidation of polypropylene under different oxygen pressures at 371 K and initiated by different quantities (mole kg^{-1}) of benzoyl peroxide: 1) 0.031; 2) 0.062; 3) 0.1.

At small values of $l < (D/\beta)^{1/2}$ oxidation takes place in the kinetic range. Under these conditions $[O_2] = \gamma p_{O_2}$ and $W_{O_2} = k_1 k_4^{-1/2} W_i^{1/2} \gamma p_{O_2}$: i.e. the rate of oxidation is independent of film thickness and is proportional to $W_i^{1/2}$.

When l is large, oxidation occurs in the diffusion range, is concentrated in a thin layer $l^* = (D/\beta)^{1/2}$, and occurs at

the rate $W_{O_2} = \gamma l^{-1} p_{O_2} (\beta D)^{1/2}$: i.e. it depends on D and l, and is proportional to $W_i^{1/4}$. In general the rate of oxidation is given by the formula

$$W_{O_2} = \gamma l^{-1} p_{O_2} \sqrt{\beta D} \tanh[l\sqrt{\beta/D}] \ .$$

With variation in the partial pressure of oxygen over a wider range account must be taken of the non-linear dependence of rate of oxidation on oxygen concentration, described with good approximation by the formula [34]

$$W_{O_2} = W_{max}(1 + b/[O_2])^{-1}, \ W_{max} = k_2 k_6^{-1/2} [RH] W_i^{1/2},$$
$$b = 2k_2 k_4 k_1^{-1} k_5^{-3} [PH] (\sqrt{1 + 12 k_4 k_5^{-2} k_6} - 1)^{-1}.$$

In a steady state the equation

$$\frac{p_{O_2}}{W_{O_2}} = \frac{b}{\gamma}(V_{max} - W_{O_2})^{-1} + \frac{1}{\varkappa\gamma}; \ \varkappa = 2D/l^2$$

represents the rate of oxidation in both kinetic and diffusion ranges [34]. It agrees well with experimental results (Fig. 2), and enables both diffusion and kinetic parameters $\varkappa$ and b to be determined. For powdered polypropylene of particle radius 10–15 μm we have $\varkappa = 0.2-0.3$ s^{-1} and $b = 3 \times 10^{-5}$ M. [34]

2. Lifetime of Alkyl Radicals in an Oxidising Polymer

In a hydrocarbon or a polymer undergoing oxidation alkyl radicals (R$^\cdot$, P$^\cdot$) are interconverted into peroxy-radicals ($RO_2^\cdot$, $PO_2^\cdot$). With sufficiently long chains the rates of the two processes are almost equal. Since in the liquid phase alkyl radicals react very rapidly with oxygen ($k_1 \approx 10^8$ M^{-1} s^{-1}), it follows that $[R^\cdot]/[RO_2^\cdot] \ll 1$. In isopentane with $p_{O_2} = 1$ atm at 373 K ($k_2[RH] = 5$ s^{-1} [24]), for example, $[R^\cdot]/[RO_2^\cdot] = 5 \times 10^{-6}$, while the lifetime of R$^\cdot$ radicals is only 10^{-6} s. Under these conditions alkyl radicals have time to react only with oxygen.

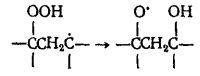
Oxygen diffuses more slowly in a polymer than in a liquid (stirring is absent, and the diffusion coefficient is smaller), so that the reaction of P$^\cdot$ with oxygen is far slower. In polypropylene with $p_{O_2} = 1$ atm at 373 K, for example, $k_1 \approx 10^6$ M^{-1} s^{-1}, [34] $\gamma = 10^{-3}$ mole kg^{-1}, [93] and the lifetime of an alkyl macroradical under these conditions is 10^{-3} s, a thousandfold the lifetime in a hydrocarbon, while the ratio $[P^\cdot]/[PO_2^\cdot] = 0.02$ on the assumption that $k_2[PH] = 5$ s^{-1} as in isopentane. As a consequence, alkyl radicals in a polymer undergoing oxidation have time not only to react with oxygen but also to undergo other reactions.

3. Role of Alkyl Macroradicals in Chain Termination

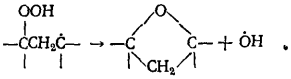
It has been shown that in polypropylene undergoing oxidation $[P^\cdot]/[PO_2^\cdot] = 0.01-0.1$ when $p_{O_2} = 0.1-1$ atm. A comparatively high relative concentration of alkyl macroradicals is present in polymers during inhibited oxidation. Inhibitors—acceptors of alkyl radicals—have a very slight effect on the oxidation of hydrocarbons [3], but inhibit that of polymers considerably more effectively [94]. For example, even at a concentration of 1mM *p*-benzoquinone inhibits the oxidation of polypropylene ($p_{O_2} = 1$ atm at 388 K), but begins to affect the oxidation of isooctane (1 atm at 353 K) only at concentrations exceeding 30mM. Moreover, such inhibitors as anthracene and 2,6-dinitrophenol, which react only with peroxy-radicals in inhibiting liquid-phase oxidation [3], terminate chains by reaction both with $PO_2^\cdot$ and with P$^\cdot$ in the oxidation of polypropylene [94]. A stable nitroxyl radical reacts with a P$^\cdot$ radical in polypropylene at 387 K and a rate constant of 35 000 M^{-1} s^{-1} (calculated from the ratio $k/k_1\gamma$ [94] with $k_1 = 1.1 \times 10^6$ M^{-1} s^{-1} and $\gamma = 10^{-3}$ M atm^{-1}). Reactions of alkyl radicals play a very important part in the formation and transformation of hydroperoxy-groups (Section IX).

IX. FORMATION AND BREAKDOWN OF HYDROPEROXY-GROUPS

In the chain oxidation of hydrocarbons all the oxygen absorbed initially forms a hydroperoxide [3]: i.e. all the $RO_2^\cdot$ radicals are converted into ROOH. In polymers a discrepancy is often observed between the quantity of oxygen absorbed and the hydroperoxide formed [46,95-97]. It has been suggested [97] that in polypropylene this is due to isomerisation of the type



or [74]



Since the reaction P$^\cdot$ + O_2 competes with isomerisation, fall in the oxygen pressure should be accompanied by decrease in the proportion of absorbed oxygen that is converted into hydroperoxide. This is supported by experiments [34] on the oxidation of polypropylene at different oxygen pressures, in which such a decrease is observed (Fig. 3). A decrease is observed also when a specimen of polypropylene is stretched and thus undergoes orientational cross-linking [98-100]. Kinetic data give for isomerisation of the peroxy-radical a rate constant of 1500 s^{-1} in polypropylene at 373 K. [34]

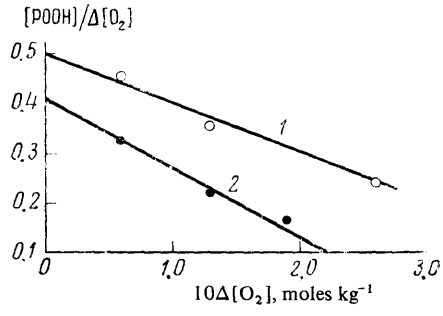
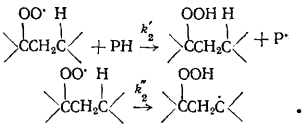


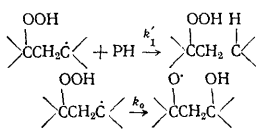
Figure 3. Dependence of $[POOH]/\Delta[O_2]$ on extent of oxidation $\Delta[O_2]$ of polypropylene initiated by benzoyl peroxide (0.064 mole kg^{-1}) at 365 K under different oxygen pressures: 1) 1 atm; 2) 0.26 atm.

Propagation of an oxidation chain in polypropylene, as in model hydrocarbons, is effected by two mechanisms—intermolecular and intramolecular—which lead to the respective formation of single and block (adjoining)

hydroperoxy-groups:



Predominantly block groups are formed in the polymer, as has been demonstrated [101] by several methods. Preferential isomerisation of peroxy-radicals characterises not only polypropylene but also hydrocarbons containing several tertiary carbon–hydrogen bonds in β positions. Thus in 2,4-dimethylpentane at 373 K the ratio $k_2'[RH]/k_2'' = 0.25$. [74] In polyethylene, in contrast, single hydroperoxy-groups are formed, as a consequence of the low probability of intramolecular isomerisation in n-alkanes. For example, in n-pentane at 373 K the corresponding ratio is 25, [102] a hundred times the value in 2,4-dimethylpentane. In a polymer the lifetime of an alkyl radical is much longer than in a liquid, and provides time for the reaction



Therefore the ratio between single and block groups (POOH and POOH') depends on the oxygen pressure:

$$\frac{[POOH]}{[POOH]'} = \frac{k_2'}{k_2''}[PH] + \frac{(k_2'[PH] + k_2'')(k_0 + k_1'[PH])}{k_1[O_2]}.$$

The proportion of block groups increases with rise in this pressure, but since they break down more rapidly into radicals, this leads to an increase in the effective rate constant of radical generation [103].

Thus through the concentration of oxygen in the polymer (polypropylene) the oxygen pressure has different effects on oxidation. Firstly, it affects the relation between the quantities of absorbed oxygen converted into POOH and into other groups:

$$\Delta[O_2]/[POOH] = 1 + k_0 k_1^{-1}[O_2]^{-1}.$$

Secondly, the ratio between the quantities of single and block POOH groups depends on the oxygen concentration and hence pressure, and this in turn affects the rate of self-initiation, since $k_{3\Sigma} = k_3[POOH]/[POOH]_\Sigma + k_3'[POOH']/[POOH]_\Sigma$. Fig. 1 shows that the higher the oxygen pressure the more rapidly does oxidation develop.

Hydroperoxy-groups are unstable, undergoing decomposition into radicals that either escape into space or undergo recombination inside the cage (with relative probabilities e and $1 - e$), as well as [34] induced chain decomposition. This last process has been demonstrated in polypropylene by an experiment involving introduction of an inhibitor and an initiator, respectively retarding and accelerating such decomposition [34]. The rate of induced chain decomposition conforms to the formula

$$W_v = \text{const} \cdot [POOH] \cdot W_i^{1/2}$$

and is consistent with the reaction scheme

$$POOH \xrightarrow{k_3} \text{Free radicals} \xrightarrow{PH} P\cdot$$
$$P\cdot + POOH \xrightarrow{k'} POH + PO\cdot$$
$$PO\cdot + PH \rightarrow P\cdot + POH \text{ (rapid)}$$
$$P\cdot + P\cdot \xrightarrow{k_4} \text{Chain termination}.$$

The rate of the chain decomposition of POOH will then be $k'k_4^{-1/2}W_i^{1/2}[POOH]$; when the hydroperoxide itself is the source of radicals, $W_i = k_3[POOH]$ and $W_v = k'k_4^{-1/2}k_3^{1/2}$ $\cdot[POOH]^{3/2}$, which agrees with experiment [34]. In polypropylene at 365 K the coefficient $k'k_4^{-1/2} = 0.02\ M^{-1/2}\ s^{-1/2}$; using the value $k_4 = 2.7 \times 10^6\ M^{-1}\ s^{-1}$, [34] we obtain $k' = 50\ M^{-1}\ s^{-1}$. Under oxidising conditions induced decomposition also takes place [34], although alkyl radicals disappear rapidly by reaction with oxygen (which is proved by comparing the rate of decomposition of POOH under oxidising conditions with its rate of decomposition into radicals).

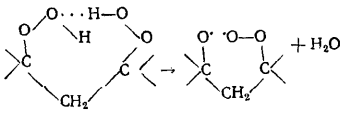
Induced decomposition must be allowed for in calculating the probability e of the escape of radicals into space. By definition $e = k_3/2k_r$, where k_r is the rate constant of breakdown into radicals. But the total rate of decomposition of POOH is $k_r[POOH] + k_v[POOH]^{3/2}$, where $k_v = k'k_4^{-1/2}k_3^{1/2}$. Calculation of e from the ratio $k_3/2k_\Sigma$ will therefore give an underestimate, since $k_\Sigma > k_r$. Hence the formula $e = k_3/2(k_\Sigma - k_v[POOH]^{1/2})$ must be used, in which k_Σ is the overall rate constant of decomposition of POOH. In polypropylene at 365 K block hydroperoxy-groups decompose with a probability $e = 0.11$ that the radicals formed will escape into space [34]; but in polyethylene at the same temperature $e = 0.5$ for the decomposition of single OOH groups [34]. Two methods—inhibitors [103] and chain oxidation [34,103]—are used to measure the formation of radicals from POOH: in the former the rate of consumption of an inhibitor W_{InH} is determined, and $W_i = fW_{InH}$ if the inhibitor is consumed only by reaction with free radicals and "captures" all the free radicals; the latter method involves measuring the rate W_{O_2} of the POOH-initiated oxidation, when $k_i = W_{O_2}^2/a^2[POOH]$, in which $a = W_{O_2}W_i^{-1/2}$ measured in an experiment with an initiator under the same conditions. Closely similar results are obtained by the two methods. If the inhibitor reacts directly with POOH, this can be taken into account in calculating k_i, but in such cases it is preferable to determine k_i from W_{O_2}, since this will give more reliable results.

Table 10. Decomposition rate constants for hydroperoxy-groups in polyethylene and polypropylene.

Polymer	Oxidation conditions	T, K	k_i, s^{-1}	Ref.
Polyethylene	in chlorobenzene at 388 K	351–403	$1.6 \cdot 10^{14} \exp(-146/RT)$	103
Polyethylene	benzoyl peroxide at 363 K	365	$5.0 \cdot 10^{-6}$	34
Polypropylene	in cumene at 388K	388	$5.0 \cdot 10^{-6}$	103
Polypropylene	in chlorobenzene at 383 K	383–413	$2.4 \cdot 10^{6} \exp(-79/RT)$	103
Polypropylene	benzoyl peroxide, 363 K, 1 atm O_2	365	$5.0 \cdot 10^{-6}$	34
Polypropylene	benzoyl peroxide, 363 K, 1 atm O_2	387	$2 \cdot 8 \cdot 10^{-5}$	34
Polypropylene	AIBN, 358 K, 1 atm O_2	322–370	$3.1 \cdot 10^{11} \exp(-119/RT)$	31

Table 10 gives values of k_i for POOH groups obtained by oxidising polypropylene and polyethylene. Comparison of k_i for the oxidation of polypropylene in cumene and in chlorobenzene, in which single and block hydroperoxy-groups respectively predominate, indicates that the latter type decompose far more rapidly [103], which is explained by the involvement of both OOH groups. By analogy with the bimolecular breakdown of POOH in the liquid phase

the most probable mechanism is



which energetically is far more advantageous that unimolecular decomposition with rupture of a single O–C bond. Furthermore, such bimolecular decomposition occurs in the liquid phase in preference to the reaction

$$ROOH + RH \rightarrow RO^{\cdot} + H_2O + R^{\cdot}$$

owing to formation of a hydrogen bond between two ROOH groups.

The mechanism of the breakdown of single hydroperoxy-groups is still obscure. Two possibilities are unimolecular decomposition at the peroxy-bond and reaction of POOH with a carbon–hydrogen bond. If radicals are generated by the latter reaction, it must be expected that $k_3^{pe} < k_3^{pp}$, since carbon–hydrogen bonds are more stable in polyethylene than in polypropylene. However, closely similar values are obtained: $k_3 = 10^{-5}$ s^{-1} in polyethylene and 0.6×10^{-5} s^{-1} for single hydroperoxy-groups in polypropylene at 398 K.[103] For a unimolecular reaction, on the other hand, k_3 should not depend on the length of the alkyl substituent and should have similar values in gaseous and condensed phases. However, it is substantially larger (hundredfold at 393 K) in liquid and solid than in the gas phase[104]. Therefore further investigation is required on the mechanism of the breakdown of POOH and ROOH in solid and liquid phases respectively.

X. CONCLUSION

As we have become convinced, the oxidation of carbon-chain polymers in the solid phase and of hydrocarbons in the liquid phase has a single mechanism—a self-initiated chain reaction involving propagation of alkyl and peroxy-radicals with bimolecular chain termination—characterised by certain kinetic features: under conditions of initiated oxidation $W_{O_2} \propto W_i^{1/2}$; at low oxygen pressures $W_{O_2} \propto p_{O_2}$ under both kinetic and diffusion régimes of oxidation; W_{O_2} is independent of sufficiently high oxygen pressures; and in the initial stage of autoxidation $\Delta[O_2] \propto t^2$. Furthermore, a solid polymer as medium in which oxidation is developing has several important characteristics, leading to the following features of chain oxidation typical only of solid-phase oxidation.

1. The free electron (as a P$^{\cdot}$ or $PO_2^{\cdot}$ macroradical) moves along the polymer in a chain oxidation mostly by a *relay mechanism* involving segmental diffusion and transfer of the electron from one segment to another by the reactions

$$P^{\cdot} + PH \rightarrow PH + P^{\cdot} \text{ и } PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot}.$$

2. As the cage walls in a polymer are formed by *slowly moving segments of macromolecules* and the form of the cage relaxes slowly, a *polymer matrix* differs from a non-polar liquid in influencing the rate of primary steps involving radicals: the more rigid the matrix, i.e. the slower are molecular displacements in it, the lower the rate of the primary step.

3. Because of the comparatively slow diffusion of oxygen in the polymer and its lower solubility *alkyl macroradicals* live for a relatively long time in the polymer, and undergo together with P$^{\cdot}$ + O_2 various other reactions, such as isomerisation, interaction with an adjacent carbon–hydrogen bond, reaction with POOH, and reactions with inhibitors effecting chain termination.

4. As a consequence of the *inhomogeneity of a polymer* different regions are oxidised at different rates. In polyethylene and polypropylene, for example, oxidation affects the amorphous phase almost alone, while the crystalline phase is oxidised only slightly.

5. Because of the *high molecular mass of a polymer* the comparatively rare (slow) *acts of rupture* of a carbon–carbon bond, which are almost imperceptible in the oxidation of the lower hydrocarbons, appear at an early stage in the oxidation of polymers.

REFERENCES

1. N. N. Semenov, "Tsepnye Reaktsii" (Chain Reactions), Goskhimizdat, Leningrad, 1934.
2. V. Ya. Shtern, "Mekhanizm Okisleniya Uglevodorodov v Gazovoi Faze" (Mechanism of the Gas-phase Oxidation of Hydrocarbons), Izd. Akad. Nauk SSSR, Moscow, 1960.
3. N. M. Emanuel', E. T. Denisov, and Z. K. Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze" (Chain Reactions in the Liquid-phase Oxidation of Hydrocarbons), Nauka, Moscow, 1965.
4. E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, "Mekhanizm Zhidkofaznogo Okisleniya Kislorod-soderzhashchikh Soedinenii" (Mechanism of the Liquid-phase Oxidation of Oxygen-containing Compounds), Nauka i Tekhnika, Minsk, 1975.
5. V. S. Pudov and A. L. Buchachenko, Uspekhi Khim., 39, 130 (1970)[Russ. Chem. Rev., No. 1 (1970)].
6. N. M. Emanuel', "Novye Rezul'taty v Oblasti Stareniya i Stabilizatsii Polimerov" (New Results on the Aging and Stabilisation of Polymers), Lecture at the "Polymers '73" Symposium, Varna, 1973.
7. W. Scott, "Atmospheric Oxidation and Antioxidants", Elsevier, Amsterdam, 1965.
8. J. Voigt, "Stabilisation of Plastics against Light and Heat" (Translated into Russian), Khimiya, Leningrad, 1972.
9. L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins", M. Dekker Inc., New York, 1969.
10. P. Yu. Butyagin, A. M. Dubinskaya, and V. A. Radtsig, Uspekhi Khim., 38, 593 (1969) [Russ. Chem. Rev., No. 4 (1969)].
11. Ya. S. Lebedev, Uspekhi Khim., 37, 934 (1968) [Russ. Chem. Rev., No. 5 (1968)].
12. A. P. Griva and E. T. Denisov, Dokl. Akad. Nauk SSSR, 219, 640 (1974).
13. A. F. Guk and V. F. Tsepalov, Kinetika i Kataliz, **14**, 322 (1973).
14. Yu. B. Shilov and E. T. Denisov, Kinetika i Kataliz, **14**, 306 (1973).
15. D. E. van Sickle, J. Polymer Sci., A-1, **10**, 355 (1972).
16. C. E. H. Bawn and S. A. Shaudhri, Polymer, **9**, 113 (1968).
17. L. Dulog and K.-H. David, Makromol. Chem., **145**, 67 (1971).

18. J. B. Lawrence and N. A. Weir, J. Appl. Polymer Sci., 18, 1821 (1974).
19. E. T. Denisov, "Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii" (Rate Constants of Homolytic Liquid-phase Reactions), Nauka, Moscow, 1971.
20. E. Niki and Y. Kamiya, Bull. Chem. Soc. Japan, 48, 3226 (1975).
21. P. I. Ivanchenko, E. T. Denisov, and V. V. Kharitonov, Kinetika i Kataliz, 12, 492 (1971).
22. A. F. Guk, S. P. Erminov, and V. F. Tsepalov, Kinetika i Kataliz, 13, 86 (1972).
23. L. Dulog and K.-H. David, Makromol. Chem., 177, 1717 (1976).
24. T. G. Degtyareva, Candidate's Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, 1972.
25. V. F. Tsepalov, Kinetika i Kataliz, 12, 1137 (1971).
26. E. Niki and Y. Kamiya, J. Org. Chem., 38, 1403 (1973).
27. S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-phase Unimolecular Reactions", Washington, 1970.
28. N. V. Zolotova and E. T. Denisov, Vysokomol. Soed., 11A, 946 (1969).
29. O. N. Karpukhin, T. V. Pokholok, and V. Ya. Shlyapintokh, Vysokomol. Soed., 13A, 22 (1971).
30. A. P. Griva, L. N. Denisova, and E. T. Denisov, Vysokomol. Soed., 19A, 219 (1977).
31. V. A. Roginskii, E. L. Shanina, and V. B. Miller, Dokl. Akad. Nauk SSSR, 227, 1167 (1976).
32. H. C. Haas, J. Polymer Sci., 55, 33 (1961).
33. Yu. B. Shilov, A. P. Griva, and E. T. Denisov, Kinetika i Kataliz, 17, 1465 (1976).
34. E. T. Denisov, Vysokomol. Soed., 19A, 1244 (1977).
35. J. C. W. Chien and D. S. T. Wang, Macromolecules, 8, 920 (1975).
36. R. Rado, D. Shimunkova, and L. Malyak, Vysokomol. Soed., 4A, 304 (1962).
37. A. V. Tobolsky, P. M. Norling, N. H. Frick, and H. Yu, J. Amer. Chem. Soc., 86, 3925 (1964).
38. Yu. B. Shilov and E. T. Denisov, Vysokomol. Soed., 14A, 2385 (1972).
39. E. Niki, C. Decker, and F. R. Mayo, J. Polymer Sci., 11, 2813 (1973).
40. Yu. B. Shilov and E. T. Denisov, Vysokomol. Soed., 11A, 1812 (1969).
41. C. Decker and F. Mayo, J. Polymer Sci., Chem. Ed., 11, 2847 (1973).
42. C. Decker, F. Mayo, and H. Richardson, J. Polymer Sci., Chem. Ed., 11, 2879 (1973).
43. S. Ya. Pshezhetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, "EPR Svobodnykh Radikalov v Radiatsionnoi Khimii" (Electron Spin Resonance of Free Radicals in Radiation Chemistry), Khimiya, Moscow, 1972.
44. A. E. Semenchenko, V. M. Solyanikov, and E. T. Denisov, Neftekhimiya, 11, 555 (1971).
45. T. A. Bogaevskaya, B. A. Gromov, V. B. Miller, T. V. Monakhova, and Yu. A. Shlyapnikov, Vysokomol. Soed., 14A, 1552 (1972).
46. T. V. Monakhov, T. A. Bogaevskaya, V. A. Gromov, and Yu. A. Shlyapnikov, Vysokomol. Soed., 16B, 702 (1974).
47. S. G. Kiryushkin and Yu. A. Shlyapnikov, Vysokomol. Soed., 16B, 702 (1974),
48. M. B. Neiman, Uspekhi Khim., 33, 28 (1964) [Russ. Chem. Rev., No. 1 (1964)].
49. A. B. Nalbandyan and A. A. Mantashyan, "Elementarnye Protsessy v Medlennykh Gazofaznykh Reaktsiyakh" (Primary Processes in Slow Gas-phase Reactions), Izd. Akad. Nauk Arm. SSR, Erevan, 1975.
50. A. M. North, "The Collision Theory of Chemical Reactions in Liquids", Methuen, London, 1964.
51. E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 51 (1976).
52. N. V. Zolotova and E. T. Denisov, Zhur. Fiz. Khim., 46, 2008 (1972) [Russ. J. Phys. Chem., No. 8 (1972)].
53. A. P. Griva and E. T. Denisov, J. Polymer Sci., 14, 1051 (1976).
54. A. P. Griva, L. N. Denisova, and E. T. Denisov, Dokl. Akad. Nauk SSSR, 232, 1343 (1977).
55. V. S. Pudov, L. L. Yasina, and A. L. Buchachenko, Kinetika i Kataliz, 15, 1110 (1974).
56. V. K. Ermolaev, Yu. N. Molin, and N. Ya. Buben, Kinetika i Kataliz, 3, 58, 315 (1962).
57. A. I. Mikhailov, Ya. S. Lebedev, and N. Ya. Buben, Kinetika i Kataliz, 6, 48 (1965).
58. B. T. Kelly, "Irradiation Damage to Solids", Permagon Press, London, 1965.
59. A. I. Mikhailov, A. I. Bol'shakov, Ya. S. Lebedev, and V. I. Gol'danskii, Fiz. Tverd. Tela, 14, 1172 (1972).
60. O. N. Karpukhin and T. V. Pokholok, Vysokomol. Soed., 15A, 2210 (1973).
61. E. T. Denisov and L. N. Denisova, Internat. J. Chem. Kinetics, 8, 123 (1976).
62. L. N. Denisova, N. Ya. Shafikov, and E. T. Denisov, Dokl. Akad. Nauk SSSR, 213, 376 (1973).
63. L. N. Denisova and E. T. Denisov, Kinetika i Kataliz, 17, 596 (1976).
64. T. G. Degtyareva, L. N. Denisova, and E. T. Denisov, Kinetika i Kataliz, 13, 1400 (1972).
65. N. Ya. Shafikov, L. N. Denisova, and E. T. Denisov, Kinetika i Kataliz, 16, 872 (1975).
66. N. M. Emanuel' and A. B. Gagarina, Uspekhi Khim., 35, 619 (1966) [Russ. Chem. Rev., No. 4 (1966)].
67. O. E. Yakimchenko, S. G. Kiryushkin, G. B. Pariiskii, D. Ya. Toptygin, Yu. A. Shlyapnikov, and Ya. S. Lebedev, Izv. Akad. Nauk SSSR, Ser. Khim., 2255 (1975).
68. O. E. Yakimchenko, I. S. Gaponova, V. M. Gol'dberg, G. B. Pariiskii, D. Ya. Toptygin, and Ya. S. Lebedev, Izv. Akad. Nauk SSSR, Ser. Khim., 354 (1974).
69. A. I. Mikhailov, S. I. Kuzina, A. F. Lukovnikov, and V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 204, 383 (1972).
70. E. R. Klinshpont and V. K. Milinchuk, Vysokomol. Soed., 17B, 358 (1975).
71. J. C. W. Chien and C. R. Boss, J. Polymer Sci., A-1, 3091 (1967).
72. V. A. Radtsig and M. M. Rainov, Vysokomol. Soed., 18A, 2022 (1976).
73. P. Yu. Butyagin, I. V. Kolbanov, A. M. Dubinskaya, and M. U. Kislyuk, Vysokomol. Soed., 10A, 2265 (1968).
74. T. Mill and G. Montorsi, Internat. J. Chem. Kinetics, 5, 119 (1973).
75. P. A. Ivanchenko, V. V. Kharitonov, and E. T. Denisov, Kinetika i Kataliz, 13, 218 (1972).
76. J. Marchal and L. Valko, Compt. rend., 272C, 2042 (1971).
77. S. E. Bresler and B. D. Erusalimskii, "Fizika i Khimiya Makromolekul" (Physics and Chemistry of Macromolecules), Nauka, Leningrad, 1965.

78. P. Yu. Butiagin, Pure Appl. Chem., 30, 57 (1972).
79. V. S. Pudov, Vysokomol. Soed., **14B**, 714 (1972).
80. Yu. B. Shilov and E. T. Denisov, Dokl. Akad. Nauk SSSR, **226**, 887 (1976).
81. E. T. Denisov, Kinetika i Kataliz, **15**, 1422 (1974).
82. V. A. Roginskii and V. B. Miller, Dokl. Akad. Nauk SSSR, **215**, 1164 (1974).
83. G. P. Voskerchyan and Ya. S. Lebedev, Izv. Akad. Nauk SSSR, Ser. Khim., 1378 (1976).
84. S. E. Bresler, E. N. Kazbekov, V. I. Formichev, F. Seg, and P. Smeitek, Fiz. Tverd. Tela, **5**, 675 (1963).
85. P. Yu. Butyagin, I. V. Kolbanev, A. M. Dubinskaya, and M. U. Kislyuk, Vysokomol. Soed., **10A**, 2265 (1968).
86. P. Yu. Butyagin, Dokl. Akad. Nauk SSSR, **165**, 103 (1965).
87. S. I. Ohnishi and I. Nitta, J. Polymer Sci., **38**, 441 (1959).
88. J. A. Kerr and M. J. Parsonage, "Evaluated Kinetic Data on Gas-phase Hydrogen Transfer Reaction of Methyl Radicals", Butterworth, London, 1976.
89. P. Neudörfl, Kolloid-Z., **224**, 132 (1968).
90. P. Yu. Butyagin, Vysokomol. Soed., **16A**, 63 (1974).
91. C. R. Boss and J. C. W. Chien, J. Polymer Sci., **A-1**, 4, 1543 (1966).
92. B. A. Gromov, Yu. A. Zubov, S. G. Kiryushkin, A. P. Mar'in, N. Ya. Rapoport, V. I. Selikova, and Yu. A. Shlyapnikov, Vysokomol. Soed., **15B**, 580 (1973).
93. R. C. Giberson, J. Polymer Sic., **A-2**, 4965 (1964).
94. Yu. B. Shilov and E. T. Denisov, Vysokomol. Soed., **16A**, 1736 (1974).
95. L. Dulog, J. K. Weise, and W. Kern, Makromol. Chem., **118**, 66 (1968).
96. T. V. Monakhova, T. A. Bogaevskaya, and Yu. A. Shlyapnikov, Vysokomol. Soed., **17A**, 1243 (1975).
97. S. G. Kiryushkin and Yu. A. Shlyapnikov, Dokl. Akad. Nauk SSSR, **220**, 1364 (1975).
98. N. Ya. Rapoport, S. I. Berulava, A. L. Kovarskii, I. N. Musaelyan, Yu. A. Ershov, and V. B. Miller, Vysokomol. Soed., **17A**, 2521 (1975).
99. N. Ya. Rapoport, N. M. Livanova, and V. B. Miller, Vysokomol. Soed., **18A**, 2045 (1976).
100. N. Ya. Rapoport and V. B. Miller, Vysokomol. Soed., **18A**, 2343 (1976).
101. J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, J. Polymer Sci., **A-1**, 6, 381 (1968).
102. D. E. van Sickle, T. Mill, F. R. Mayo, H. Richardson, and C. W. Gould, J. Org. Chem., **38**, 4435 (1973).
103. N. V. Zolotova and E. T. Denisov, J. Polymer Sci., **A-1**, 9, 3311 (1971).
104. E. T. Denisov, Zhur. Fiz. Khim., **49**, 2473 (1975) [Russ. J. Phys. Chem., No. 10 (1975)].

Institute of Chemical Physics,
USSR Academy of Sciences,
Chernogolovka