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Oxidative Polymerisation of Vinyl Monomers

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The results of studies on the kinetics and mechanism of the oxidative polymerisation and copolymerisation of vinyl monomers are described systematically and discussed critically. Attention is concentrated on the elucidation of the relation between the structure and reactivity of the monomers in oxidative polymerisation and on the role of oxygen as an inhibitor in the free-radical chain polymerisation.
The bibliography includes 139 references.

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I. INTRODUCTION

Radical polymerisation in the presence of oxygen, called oxidative polymerisation †, is accompanied by oxidation which results in the formation of low-molecular-weight products with oxygen-containing functional groups (aldehydes, ketones, etc.) in addition to the copolymers with oxygen. The specific features and characteristics of the simultaneous occurrence of polymerisation and oxidation have been the subject of numerous investigations, which have led to the establishment (mainly during the last three decades) of oxidative polymerisation as an independent field of radical-chain polymerisation.

The study of the role of oxygen in radical polymerisation, begun by Lebedev[4] and Staudinger[5] and continued mainly by Medvedev[6], Bovey and Kolthoff[7], and Barns et al.[8], enabled Schulz and Henrici[2], Mayo et al.[9], and Kern[10], to establish the principal features of the mechanism of the oxidative polymerisation of compounds of the vinyl type ‡.

† The term "oxidative polymerisation" is used in the literature usually for the polymerisation of monomers (oligomers) in the presence of O_2 when initiation is achieved as a result of degenerate branching by peroxides (hydroperoxides)[1]. On the other hand, if the initiator is introduced from outside, and degenerate branching does not play a significant role in initiation, the process is called "inhibited polymerisation"[2] or "oxidation"[3]. We believe it to be more logical and rigorous in relation to the reaction mechanism to extend the term "oxidative polymerisation" to all instances of the polymerisation of unsaturated compounds in the presence of oxygen, regardless of the method of initiation.

‡ Compounds of the vinyl type, whose C–O bonds are activated by $\pi-\pi$ conjugation or by electron-donating or electron-accepting substituents [-CN, C(O)-, -C(O)–O, Cl, , etc.] in the α-position relative to the double bond, are considered. Compounds containing the $CH_3-CH=CH-$, $CH_2=CH-CH_2-$, $CH_2-CH=CH$, and $CH_2=CH-CH$ structural units, in which the substituents in the α-position with respect to the relatively inactive C = C bond are the methyl, methylene, or methylidyne groups, exhibiting a weak electron-donating capacity, are included with allyl compounds[9,11,12].

Studies[13–16] were unable to determine the mechanism of the formation of hydroperoxide and the generation of oxidation chains for compounds of the allyl type. However, the formation of hydroperoxides is most probably only one of the reactions involving the formation of polymers from allyl compounds in the presence of oxygen. On the whole, this process has remained little studied for compounds of the allyl type.

During recent years, there has been a sharp increase of interest in polymerisation in the presence of oxygen. This is associated with the current development of fundamentally new methods for the formation of organic coatings using monomers[17,18] and also with the fact that oxidative polymerisation constitutes the basis for the formation of films of unsaturated compounds. The theoretical aspect of the study of the interaction between oxygen and unsaturated compounds involves the fundamental problem of the relation between the structure and reactivity of organic compounds in radical addition and substitution reactions.

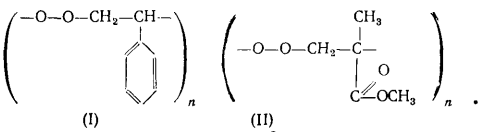
The available review publications are devoted mainly to the chemistry of polymeric peroxides[19–21] with the exception of a recent study in the field of the history of science[22], which reflects fairly completely the establishment of the field of oxidative polymerisation. It has now become necessary to survey and analyse critically studies dealing with the formation of polymers as a result of the interaction of unsaturated compounds with oxygen, to examine the present state of the field of oxidative polymerisation, to deduce the principle trends in its development, and to discover promising pathways to be followed in future research. Such an attempt is made in the present review.

II. KINETICS AND MECHANISM OF OXIDATIVE POLYMERISATION

1. Mono-unsaturated Compounds

Studies on the oxidative polymerisation of styrene[23–26], α-methylstyrene[27], and methyl methacrylate[2,3] have been of fundamental importance for the elucidation of the mechanism of the interaction of vinyl monomers with oxygen. The key to the understanding of the process mechanism has been the isolation[7,8,28] of polymeric peroxides derived

from styrene (I) and methyl methacrylate (II) and the determination of their structure as regular copolymers formed by the interaction of monomers with oxygen:

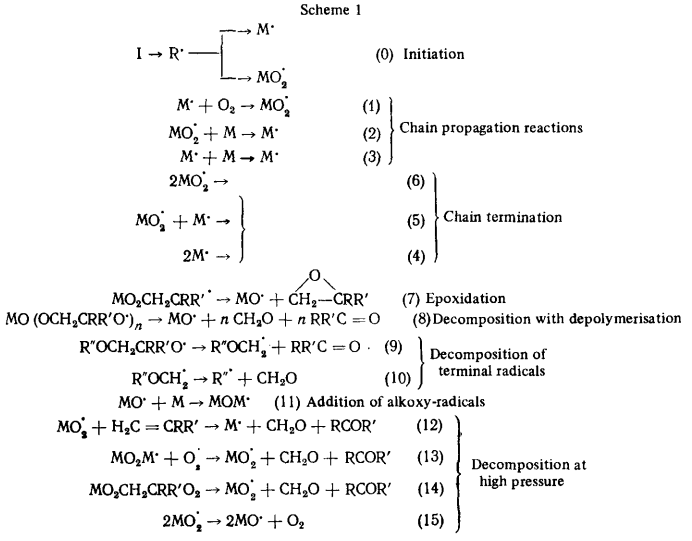


(I) (II)

It is noteworthy that Staudinger[29] was the first to identify a polymeric peroxide as the product of the interaction of 1,1-diphenylethylene with oxygen.

Styrene. The reaction of styrene with oxygen leads to the formation of a polyperoxide, benzaldehyde, formaldehyde, and styrene oxide (phenyloxiran), the aldehydes being formed in equimolar amounts simultaneously with the polyperoxide from the very lowest degrees of conversion[24,30]. The mechanism of the oxidative polymerisation of styrene [Scheme (1)], proposed by Mayo[25], provides a good explanation of the nature of the accumulation of the reaction products as a function of the partial pressure of oxygen (P_{O_2}) (see Figure). The polyperoxide and low-molecular-weight products are formed as a result of the addition, isomerisation, and decomposition of the radicals M$^{\cdot}$, $MO_2^{\cdot}$, and MO$^{\cdot}$ (I is the initiator).

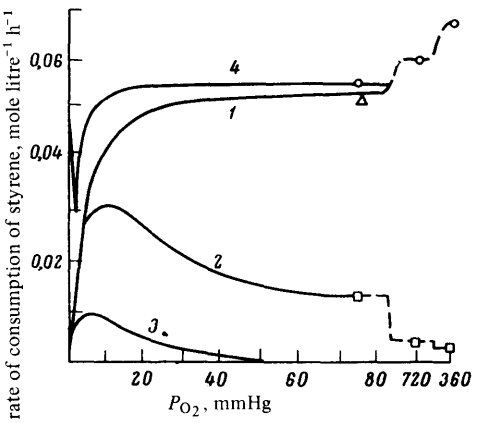
Scheme 1



The formation of the polymeric peroxide by reactions (0), (1), (2), and (6) in the range of oxygen pressures 160 to 3100 mmHg is consistent with kinetic results[24-26]. The rate of consumption of oxygen (W_{O_2}) obeys the equation

$$W_{O_2} = \frac{k_2}{k_6^{1/2}} \cdot k_i^{1/2} [M] [I]^{1/2} \qquad (I)$$

(where M, I, k_i, k_2, and k_6 are respectively the monomer, the initiator, and the initiation, chain propagation, and chain termination rate constants), which follows from the set of elementary reactions with the rate-limiting stage (2), indicated in scheme (1). In this oxygen pressure range W_{O_2} is independent of P_{O_2} and quadratic chain termination takes place at peroxy-radicals, the main reaction product is the polyperoxide, and the yield of low-molecular-weight compounds (phenyloxiran, CH_2O, and benzaldehyde) is approximately 3% (see Figure). Low-molecular-weight compounds are formed in the decomposition of radicals $MO_2^{\cdot}$ and $MO_2M^{\cdot}$ via reactions (11)-(14), whose rate is independent of P_{O_2}. Since $k_1/k_3 = 4.4 \times 10^6$ (at 50°C), all the radicals M$^{\cdot}$ are in fact converted into $MO_2^{\cdot}$ via reaction (1) before they can react with the monomer via reaction (3). The contribution of the MOOM$^{\cdot}$ radical decomposition reaction (7), which also competes with reaction (1), is small judging from the yields of the alkoxy-radicals and phenyloxiran at P_{O_2} = 3200 - 100 mmHg. Correspondingly the aldehyde formation reactions (8)-(10) do not play a significant role. This ensures the formation of the polyperoxide as the main product of the interaction of styrene and oxygen at $P_{O_2} \geq 100$ mmHg.



Dependence of the rates of formation of products in the oxidative polymerisation of styrene on the oxygen pressure[25]: *1*) polymeric peroxide; *2*) benzaldehyde and formaldehyde; *3*) phenyloxiran; *4*) overall rate of consumption of styrene; temperature -50°C; concentration of azobisisobutyronitrile 0.01 M.

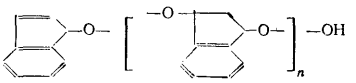
With decrease in the partial pressure of oxygen (particularly at P_{O_2} = 80 - 10 mmHg), the rate of formation of the polyperoxide diminishes and the yield of phenyloxiran and the aldehydes increases (see Figure). A decreased concentration of dissolved oxygen increases the lifetime of the radicals $MO_2M^{\cdot}$: $\tau = 1/k_1[O_2]$. This produces an increase in the rate of reaction (3) and in the rates of the isomerisation reaction (7) and the depolymerisation reactions (8)-(10), which gradually displace the polyperoxide formed. Since reaction (7) proceeds with an activation energy E_7 = 8-10 kcal mole^{-1}, [31] while reactions (1) and (3) which compete with it have $E_1 = 0$ and E_3 = 6-7 kcal mole^{-1}, [32] an increase of temperature causes, like a decrease of P_{O_2}, an increased yield of phenyloxiran and aldehydes compared with the formation of the polyperoxide. It has been shown[33] that under certain conditions {100-120°C, P_{O_2} = 160-80 mmHg, [M] = 10-40 vol.%} only oxidative-degradative reactions of styrene take place with formation of phenyloxiran and aldehydes, while the polymeric pathway in the interaction of styrene with oxygen is almost entirely suppressed.

When $P_{O_2} = 5-1$ mmHg, the cross-termination reaction (5) becomes dominant: $W_{O_2} \propto [M]^{1/2}[O_2]^{1/2}$: irregularities of the type ~M–M~, which hinder the depolymerisation reactions (8) and (9) and lower the yield of aldehydes, are encountered in polymer chains with increasing frequency. The rate of formation of phenyloxiran also decreases in view of the decrease of the fraction of ~MOOM~ units owing to the formation of ~MM~ and the overall rate of consumption of styrene falls sharply, since $k_5 \gg (k_4k_6)^{1/2}$. In the absence of oxygen ($P_{O_2} = 0$) polystyrene is formed by reactions (0), (3), and (4).

In terms of its most important features, the mechanism of oxidative polymerisation established for styrene proved to be valid for vinyl monomers such as α-methylstyrene[27,34-37] and methyl methacrylate[2,3,38,39].

Indene. The double bond activated by the aromatic ring and the methylene group in the α-position relative to the double bond are responsible for the ability of indene to interact with oxygen to form both hydroperoxides and polyperoxides[40,41]. Under mild conditions, the oxidation of indene leads to the formation of a hydroperoxide which is unstable above 40° C and is converted into carbonyl compounds[42].

Russell carried out a chemical and kinetic study of the oxidative polymerisation of indene[43,44], which established the structure of the polyperoxide:



and the mechanism of its formation via the reactions in Scheme 2.

Scheme 2

$$I \rightarrow R^{\cdot} \xrightarrow[M]{O_2} MO_2^{\cdot}, \quad (0)$$

$$M + O_2 \xrightarrow{k_{O'}} MO_2^{\cdot}, \quad (0')$$

$$M^{\cdot} + O_2 \xrightarrow{k_1} MO_2^{\cdot}, \quad (1)$$

$$MO_2^{\cdot} + M \xrightarrow{k_2} M^{\cdot}, \quad (2)$$

$$MO_2^{\cdot} + MH \xrightarrow{k_{2'}} MO_2H + M^{\cdot}, \quad (2')$$

$$2MO_2^{\cdot} \rightarrow \text{non-radical products.} \quad (6)$$

In contrast to styrene and methyl methacrylate, initiation reactions via the direct interaction of the monomer and oxygen [reaction (O')] and chain transfer reactions as a result of the elimination of hydrogen from the α-methylene group by the peroxy-radical [reaction (2')] play a significant role in the oxidative polymerisation of indene. The fact that the rate of the overall reaction obeys the equation

$$W_{O_2} = \frac{k_2 + k_{2'}}{k_6^{1/2}}[M](k_i[I] + k_{O'}[M])[O_2])^{1/2} \quad (II)$$

may be regarded as kinetic proof of the validity of the above scheme.

Thermal oxidative polymerisation has been investigated for styrene[23,45], methyl methacrylate[46], n-butyl methacrylate[47], and indene[44]. The rate of reaction obeys the equation

$$W_{O_2} = k[M]^n [O_2]^m \quad (III)$$

with values of n and m (Table 1) close to the theoretical values: $n = 1.5$ and $m = 0.5$. This enabled Mayor and Russell to assume that the reaction proceeds via Scheme 3, from which it follows that $k = k_i^{1/2}k_2/k_6^{1/6}$ in the above equation.

Scheme 3

$$M + O_2 \xrightarrow{k_{O'}} M^{\cdot}, \quad (0)$$

$$M^{\cdot} + O_2 \xrightarrow{k_1} MO_2^{\cdot}, \quad (1)$$

$$MO_2^{\cdot} + M \xrightarrow{k_2} M^{\cdot}, \quad (2)$$

$$2MO_2^{\cdot} \xrightarrow{k_6} \text{non-radical products.} \quad (6)$$

Chain initiation in vinyl compounds apparently proceeds as a result of the addition of oxygen to the double bond via the reaction[48,49]

$$C_6H_5CH{=}CH_2 + O_2 \rightarrow C_6H_5{-}\dot{C}H{-}CH_2OO^{\cdot}.$$

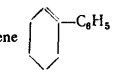
Table 1. Characteristics of oxidative thermal polymerisation of monomers.

Monomer	Reaction order w.r.t. monomer (n)	Reaction order w.r.t. oxygen (m)	Refs.	Monomer	Reaction order w.r.t. monomer (n)	Reaction order w.r.t. oxygen (m)	Refs.
Styrene	1.38	0.37	23	Indene	1.50	0.50	44
Styrene	1.78	0.34	45	Methyl methacrylate	1.70	0.47	46

The thermal oxidative polymerisation of styrene and n-butyl methacrylate at 50° C proceeds at rates smaller by a factor of 3–4 than in initiated oxidative polymerisation[23,45,47] owing to the low rates of initiation and degenerate branching of the chain by the polymeric peroxides.

In contrast to styrene, α-methylstyrene, methyl methacrylate, and indene, the oxidative polymerisation of other monomers of the vinyl type, such as chain-substituted[9,27,44] and ring-substituted[50] styrene, acrylonitrile[9,51-56] and its derivatives[54,57,58], methacrylates[39,59-64] and acrylates[46,57,63,65], vinyl acetate[9,57,66], and halogenoethylenes[67-76], has been studied much less. The kinetics of the interaction of oxygen with all the monomers investigated obey Eqn. (I). The influence of the medium is manifested by the fact that an increase in the dielectric constant of the solvent leads to an increase of the rate of reaction[59,60]. It follows from the kinetic data that the initiated oxidative polymerisation of compounds with activated π bonds proceeds via a mechanism incorporating the elementary reactions (0), (1), (2), and (6) (Scheme 1), in the region of oxygen pressures where the rate of reaction is independent of P_{O_2}. The copolymerisation of monomers with O_2, leading to the formation of polymeric peroxides, takes place via the chain propagation reactions (1) and (2) (Scheme 1). The comparatively few kinetic characteristics of the formation of polyperoxides are presented in Tables 2 and 3 (see also Table 6).

Table 2. Kinetic characteristics of the oxidative polymerisation of certain monomers.

Medium	Temp. °C	$10^3 k_2/k_6^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$	$k_2/k_6^{1/2}$ = A exp (−E/RT)	Refs.
Styrene $CH_2=CHC_6H_5$				
Styrene	35	5.6	$k_2/k_6^{1/2}=6.8\cdot10^4\cdot\exp\left(-\frac{10\,000}{RT}\right)$	23*
	50	11.6		
	65	24.4		
Styrene	45	13.3	$k_2/k_6^{1/2}=2.4\cdot10^3\exp\left(-\frac{7700}{RT}\right)$	77
	50	16.5		
	55	18.8		
	60	22.8		
	70.5	32.0		
Styrene	35	6.8	$k_2/k_6^{1/2}=(5,8\pm0.3)\cdot10^3\cdot\exp\left(-\frac{8300}{RT}\right)$	46
	40	8.8		
	45	10.7		
	50	13.7		
	60	20.0		
α-Methylstyrene $CH_2=C(CH_3)-C_6H_5$				
Chlorobenzene	13	6.2	$k_2/k_6^{1/2}=(3.5\pm0.2)\cdot10^2\cdot\exp\left(-\frac{6170\pm300}{RT}\right)$	79
	30	13.0		
	40	15.5		
	50	23.0		
β-Methylstyrene $(CH_3)CH=CH-C_6H_5$				
β-Methylstyrene	50	5.65		27*
α-Phenylstyrene $CH_2=C-(C_6H_5)_2$				
α-Phenylstyrene	50	4.87		9*
		6.40		44*
β-Bromostyrene $CH(Br)=CH-C_6H_5$				
β-Bromostyrene	50	0.02		9*
Acrylonitrile $CH_2=CH-CN$				
Acrilonitrile	35	0.87	$k_2/k_6^{1/2}=(57\pm2)\cdot10^3\exp\left(-\frac{11\,000}{RT}\right)$	56
	40	1.21		
	45	1.62		
	50	2.20		
	55	2.75		
Substituted acrylonitriles $CH_2=C(R)-CN$ (in chlorobenzene)				
Methylacrylonitrile	50	4.60		54*
Ethylacrylonitrile	50	3.42		
n-Propylacrylonitrile	50	2.79		
Isopropylacrylonitrile	50	2.54		
n-Pentylacrylonitrile	50	2.44		
Methyl methacrylate $CH_2=C(CH_3)C(O)-OCH_3$				
Methyl methacrylate	30	0.61	$k_2/k_6^{1/2}=(17.4\pm1.0)\cdot10^3\cdot\exp\left(-\frac{10\,500}{RT}\right)$	39
	40	0.79		
	45	1.03		
	50	1.42		
	60	2.35		
***n*-Butyl methacrylate $CH_2=C(CH_3)C(O)-OC_4H_9$**				
n-Butyl methacrylate	50	1.22	$k_2/k_6^{1/2}=(4.57\pm0.1)\cdot10^4\exp\left(-\frac{11\,200\pm800}{RT}\right)$	3
	65	2.56		
	80	5.30		
	35	0,60	$k_2/k_6^{1/2}=(6.7\pm0.5)\cdot10^3\cdot\exp\left(-\frac{10\,000}{RT}\right)$	39
	40	0,70		
	50	1,19		
	60	1,90		
n-Nonyl methacrylate $CH_2=C(CH_3)C(O)-O(CH_2)_8-CH_3$				
n-Nonyl methacrylate	50	1.32	$k_2/k_6^{1/2}=(33.9\pm9.0)\cdot10^3\cdot\exp\left(-\frac{11\,000}{RT}\right)$	39
	60	1.65		
	70	3.09		
	80	5.10		
n-Cetyl methacrylate $CH_2=C(CH_3)C(O)-O(CH_2)_{15}-CH_3$				
n-Cetyl methacrylate	50	1.08	$k_2/k_6^{1/2}=(6,4\pm0.7)\cdot10^3\cdot\exp\left(-\frac{10\,000}{RT}\right)$	39
	60	1.70		
	70	3.02		
	80	3.70		
	90	5.53		
Methyl acrylate $CH_2=CH-C(O)-OCH_3$				
Methyl acrylate	40	0,35	$k_2/k_6^{1/2}=(1.0\pm0.1)\cdot10^3\cdot\exp\left(-\frac{9400}{RT}\right)$	65
	50	0.42		
n-Butyl acrylate $CH_2=CH-C(O)-OC_4H_9$				
n-Butyl acrylate	50	0.47	$k_2/k_6^{1/2}=(0.18\pm0.02)\cdot10^3\cdot\exp\left(-\frac{8200}{RT}\right)$	65
	60	0.79		
	70	1.05		
	80	1.49		
n-Nonyl acrylate $CH_2=CHC(O)-O(CH_2)_8CH_3$				
n-Nonyl acrylate	50	0.42	$k_2/k_6^{1/2}=(1.36\pm0.10)\cdot10^3\cdot\exp\left(-\frac{9600}{RT}\right)$	46
	60	0.60		
	70	1.01		
	80	1,57		
Methyl vinyl ketone $CH_2=C-C(O)-CH_3$				
Methyl vinyl ketone	40	0,70	$k_2/k_6^{1/2}=(201\pm13)\cdot10^3\cdot\exp\left(-\frac{13\,500}{RT}\right)$	46
	45	1.07		
	50	1,38		
Vinyl acetate $CH_2=CHOC(O)-CH_3$				
Vinyl acetate	35	0,30	$k_2/k_6^{1/2}=(0,23\pm0,07)\cdot10^3\cdot\exp\left(-\frac{8300}{RT}\right)$	66
	40	0.41		
	45	0,51		
	50	0.61		
Tetrafluoroethylene $CF_2=CF_2$				
Water	40—70		$k_2/k_6^{1/2}=65\cdot\exp\left(-\frac{1200}{RT}\right)$	75
Indene 				
Indene	50	17,5		44
Phenylcyclohex-1-ene 				
Chlorobenzene	25	—	$k_2/k_6^{1/2}=9,1\cdot10^3\cdot\exp\left(-\frac{8400\pm300}{RT}\right)$	80, 81
	50	18		
	60	31		
	70	42		
	80	58		
Buta-1,3-diene $CH_2=CH-CH=CH_2$				
Butadiene	30	1.21	$k_2'/k_6^{1/2}=(10.3\pm1.1)\cdot10^3\cdot\exp\left(-\frac{13\,700}{RT}\right)$	82
	40	2.92		
	50	4.80		
Benzene	60	8.8		
Chloroprene $CH_2=CH-CCl=CH_2$				
Chloroprene	0	27.7	$k_2/k_6^{1/2}=2.65\cdot10^3\cdot\exp\left(-\frac{9600}{RT}\right)$	55
	20	92.8		
	35	207.6		

* The values of $k_2/k_6^{1/2}$ were calculated by the expression $k_2/k_6^{1/2} = W_{O_2}/[M]k_i[\bar{A}BIBN]^{1/2}$ from the rates of oxidative polymerisation W_{O_2} quoted in the relevant studies. The rate constants k_i for initiation by azobisisobutyronitrile (ABIBN) were taken from Tüdos[83] for styrene and its derivatives, from Turesanye and Tüdos[84] for vinyl acetate, from the same paper for acrylonitrile and its derivatives, from Sukhov and coworkers[46,85] for methacrylate and acrylate esters, from Turesanye and Tüdos[84] for methyl vinyl ketone, isopropenyl methyl ketone, and isopropenyl acetate, from Van Hook and Tobolsky[86] and Hammond et al.[87] for butadiene, and from Bailey[55] for chloroprene.

The structure of the polymeric peroxides corresponds to the formula -M-OO- when the monomer M reacts with oxygen under conditions (in terms of the O_2 concentration) ensuring quadratic chain termination by $\sim MO_2^{\cdot}$ radicals. The structure of the polymeric chains and peroxides with a regular alternation of -M- and -O-O- units constitutes independent confirmation of the validity of the mechanism of their formation under discussion. The extremely limited information about the structure of polymeric peroxides and some of their properties have been largely reviewed in Refs. 19–21 and 88.

Judging from the products formed, it is most likely that the thermal decomposition of the polymeric peroxides derived from styrene[24], α-methylstyrene[27], methyl methacrylate[38] n-butyl methacrylate[62], acrylonitrile[52], methacrylonitrile[53], vinyl chloride[68], and tetrafluoroethylene[73-75] proceeds via a free-radical chain mechanism.

In the oxidative polymerisation of vinyl compounds via the mechanism illustrated in Scheme 1 chain propagation takes place via the addition reaction (2). Together with addition to the double bond, the peroxy-radical can participate in the homolytic substitution reaction (2′) in Scheme 2, abstracting hydrogen from a monomer molecule. Polymeric peroxides, aldehydes, ketones, and epoxides are formed via the addition reaction[9], while hydroperoxides, alcohols, carbonyl compounds, and acids with the same number of carbon atoms as the initial olefin are formed via the substitution reaction[31,89]. On the basis of the study of the reaction products, Mayo et al.[9] concluded that the addition reaction predominates when the double bond is conjugated with aromatic, vinyl, carbonyl, or nitrile groups or when the saturated compound does not contain an allylic hydrogen atom. According to Buckley and Szwarc[90], the reactivity of unsaturated compounds as free radical acceptors increases sharply when their double bonds are activated by conjugation. Indeed, hydroperoxides or other substances indicating the occurrence of the substitution reactions have not been found in the products of the interaction with oxygen of all the compounds having activated π bonds investigated to date, with the exception of indene and phenylcyclohex-1-ene. It follows from the results of studies on the joint oxidation of styrene, α-methylstyrene, and methyl methacrylate with hydrocarbons such as tetralin and cumene (Tables 4 and 5) that peroxy-radicals add predominately to the double bonds.

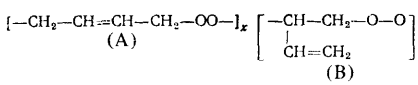
Thus the reaction involving substitution by the peroxy-radical plays a subsidiary role for vinyl compounds compared with the addition reaction. At the same time the kinetic chain is transferred to the monomer via the substitution reaction and the latter is probably largely responsible for the decrease of the length of the molecular chains of polymeric peroxides whose degree of polymerisation ($\bar{P}_n$) is as a rule comparatively low: $10 < \bar{P}_n < 30$.

Together with the competition between the substitution and addition reactions, the competition between the polymeric and oxidative pathways in the interaction of oxygen with monomers is extremely important. To date, this pathway has been studied only for styrene[25,31,33] and partly for α-methylstyrene[27,37] and methyl methacrylate[3,38].

2. Dienes and Polyenes

The mechanism of the oxidative polymerisation of hydrocarbons with conjugated double bonds has been established mainly as a result of the work of Kern and coworkers[92-95].

Buta-1,3-diene. The interaction of butadiene with oxygen in solvents gives a high yield of a polymer with $\bar{M}_n = 700-850$. This polymer is formed[96] as a result of the 1,2- and 1,4-addition of oxygen to butadiene, the latter pathway predominating:



(A) (B)

The structure of the polymer was demonstrated by its reduction with LiAlH to but-2-ene-1,4-diols and bute-3-ene-1,2-diols, the hydrogenation of which gave the corresponding butanediols. Formaldehyde and acrolein, identified in the thermal decomposition of the polymeric peroxide, corresponded to structure (B). Structure (A) was demonstrated by the formation of phenylhydrazones on treatment of the polymeric peroxide with phenylhydrazine.

Table 3. The rate constants for the elementary reactions in the oxidative polymerisation of certain monomers.

Medium	Temp., °C	k_2, litre mole^{-1} s^{-1}	$10^7 k_6$, litre mole^{-1} s^{-1}	k_2 (k_6) = $A \cdot \exp(-E/RT)$	References
Styrene					
Styrene	20	10.3	1.5		61
		9.9	1.8		
Chlorobenzene	13	19	4.8	$k_2 = (4.7 \pm 0.2) \cdot 10^7 \cdot \exp\left(-\frac{8400 \pm 300}{RT}\right)$	
	22	30	5.0		
	30	41	4.2		
	40	70	6.2	$k_6 = (1.04 \pm 0.20) \cdot 10^9 \cdot \exp\left(-\frac{1800 \pm 1200}{RT}\right)$	
	50	98	6.2		78
α-Methylstyrene					
α-Methylstyrene	20	2.2	0.015		61
Toluene		2.4	0.021		
Chlorobenzene	13	4	0.04	$k_2 = (6.6 \pm 0.7) \cdot 10^6 \cdot \exp\left(-\frac{8070 \pm 800}{RT}\right)$	
	30	10	0.06		
	40	15	0.08	$k_6 = (3.4 \pm 1.1) \cdot 10^8 \cdot \exp\left(-\frac{3700 \pm 1000}{RT}\right)$	79
	50	82	0.14		
β-Methylstyrene					
Chlorobenzene	30	51	3.2		79
Methyl methacrylate					
Methyl methacrylate	50	1.8	0.2	$k_2 = 8.3 \cdot 10^8 \cdot \exp\left(-\frac{12\,800}{RT}\right)$	63
	30	0.5	0.1	$k_6 = 2.1 \cdot 10^9 \cdot \exp\left(-\frac{4600}{RT}\right)$	
Methyl methacrylate	20	0.24	0.27	—	61
Methyl methacrylate	30	1.0	0.8	—	57
Butyl methacrylate					
Butyl methacrylate	30	0.8	0.3	$k_2 = 6.3 \cdot 10^7 \cdot \exp\left(-\frac{10\,900}{RT}\right)$	63
	50	2.8	0.4	$k_6 = 2.2 \cdot 10^8 \cdot \exp\left(-\frac{2600}{RT}\right)$	
Methyl acrylate					
Methyl acrylate	50	1.7	1.6	—	63
Butyl acrylate					
Butyl acrylate	50	1.4	9.0	—	63
Indene					
Chlorobenzene	30	128	5.0	—	79
Phenylcyclohex-1-ene					
Chlorobenzene	25	—	25		
	50	284	25		
	60	490	—	$k_2 = 1.4 \cdot 10^8 \cdot \exp\left(-\frac{8400 \pm 300}{RT}\right)$	80, 81
	70	664	—		
	80	915	—		

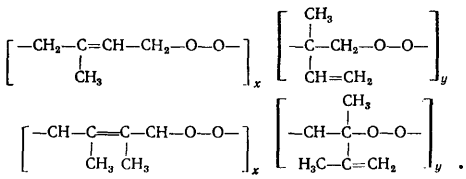
A detailed study of the initiated and thermal oxidative polymerisation of butadiene, undertaken by Mayo and coworkers[82,97], established that, in the temperature range 30–50°C, at $P_{O_2} > 40$ mmHg, and for low conversions, the main product is the polymeric peroxide $(C_4H_6O_2)_n$, consisting of equal numbers of *trans*-buta-1,2-diene and *trans*-buta-1,4-diene units connected by -O–O- bridges. Only at $P_{O_2} < 10$ mmHg is several per cent of 1-ethyloxiran (butadiene 1,2-oxide) and 1-formyloxiran (acrolein

1,2-oxide) formed. The epoxides are formed via reaction (7) in scheme 1, which had been established previously for styrene[25]:

$$\sim MO_2M^{\cdot} \xrightarrow{k_7} MO^{\cdot} + H_2C\overset{O}{\diagup\!\!\diagdown}CH{-}CH{=}CH_2 \ .$$

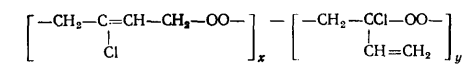
The rate of this reaction increases with decreased partial pressure of oxygen and the ratio k_1/k_7 is 3×10^{-6} and 20×10^{-6} at $P_{O_2} = 20$ and 3 mmHg respectively. The decomposition of polymeric alkoxy-radicals [reaction (8), Scheme 1] leads to acrolein: $\sim MO_2{-}MO^{\cdot} \rightarrow MO^{\cdot} + CH_2O + O{=}CH{-}CH{=}CH_2$; the radicals are formed via reaction (7) and have terminal buta-1, 2-diene units. The rate of initiation of the oxidative polymerisation of butadiene in the oxygen pressure range from 40 to 900 mmHg, where W_{O_2} is independent of P_{O_2}, obeys Eqn. (I) with the kinetic parameters listed in Table 2.

Isoprene and 2,3-dimethylbuta-1,3-diene. The available information about the interaction of oxygen with isoprene and 2,3-dimethylbuta-1,3-diene is extremely limited[92-94]. It has been shown[92-94] that the polymeric peroxides formed are regular copolymers of dienes with oxygen and have the following structure:

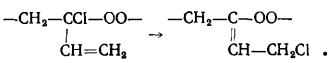


When the reaction of 2,3-dimethylbutadiene with oxygen is continued up to high conversions, hydroperoxy-groups and ether bonds appear in the polyperoxide, while α-isopropenylacrolein and dimethylglyoxal were detected in the volatile product in addition to formaldehyde and isopropenyl methyl ketone[98].

Chloroprene. The main product of the interaction of chloroprene with oxygen is a polymeric peroxide having the following structure[95,99]:



Readily hydrolysable chlorine, in amounts proportional to the amount of absorbed O_2, was detected in the polyperoxide. This led to the conclusion that oxygen undergoes 1,2-addition, which is accompanied, according to the authors[99], by the allylic rearrangement



A more detailed study of the structure of the polymeric chloroprene peroxide showed[55] that units resulting from 1,4-addition predominate. For low conversions, the kinetics of the oxidative polymerisation of chloroprene obey Eqn. (I). The principal kinetic characteristics of the process are listed in Table 2.

Thus, according to structural-chemical and kinetic data, polymeric peroxides of 1,3-dienes are formed via a mechanism incorporating the elementary reactions (0), (1), (2), and (6) (Scheme 1), the peroxy-radical adding to the monomer in the 1,4- and 1,2-positions.

The available information about the oxidative polymerisation of the *esters of acids having conjugated π bonds* is extremely limited. The addition of oxygen in the 1,2- and 1,4-positions of α-eleostearic acid has been demonstrated[100,101], the triene system of conjugated double bonds being converted into a diene system with formation of dimeric peroxy-products[102-104]. The peroxides derived from the methyl esters of octadeca-9,11-dienoic and octadeca-10,12-dienoic acids are regular 1 : 1 copolymers of the esters with oxygen whose degree of polymerisation is 2–4 [88] and which are formed as a result of the addition of polyperoxy-radicals in the 1,2- and 1.4-positions. The rate of oxidative polymerisation of the methyl esters of α-eleostearic[103] and octadeca-9,11-dienoic acids[93,105,106] obeys the equation

$$W_{O_2} = k\,[PP]^{1/2}.[M],$$

where [PP] and [M] are the concentrations of the polymeric peroxide and the monomer respectively.

This equation follows from Scheme 1 [elementary reactions (1),(2), and (6)], provided that the initiators are polyperoxides which decompose unimolecularly. The kinetics of the interaction of β-carotene (a polyene with conjugated π bonds) with oxygen were investigated and the formation of peroxides and epoxides in parallel reactions was established[107].

Table 4. The rate constants (litre mole^{-1}s^{-1}) for the reactions of certain peroxy-radicals with hydrocarbons at 30° C. [91]

Hydrocarbon	Peroxy-radical of				Average value for tertiary peroxy-radicals
	n-butane	s-butane	cyclohexane	tetralin	
Ethylbenzene	0.5	0.5	0.5	0.5	0.23
Cumene	0.4	0.4	—	0.5	0.17
Tetralin	6.4	4.2	4.5	6.3	1.7
Styrene	14	6.3	6.8	8.8	1.6
α-Methylstyrene	25	12	14	16	3.9*

* Data for cumenylperoxy-radicals.

III. OXIDATIVE COPOLYMERISATION§

The polymerisation process in a system consisting of monomers A and B and oxygen leads to the formation of ternary copolymers having the composition $(\sim AOO\sim)_n$–$(\sim BOO\sim)_m$. Chain propagation and termination proceeds via reactions in Scheme 4:

Scheme 4

$$\sim A^{\cdot}\,(\sim B^{\cdot}) + O_2 \rightarrow AO_2^{\cdot}\,(BO_2^{\cdot}) \qquad (1)$$

$$\left.\begin{aligned} \sim AO_2^{\cdot} + A &\xrightarrow{k_{AA}} \sim AOOA^{\cdot} \\ \sim AO_2^{\cdot} + B &\xrightarrow{k_{AB}} \sim AOOB^{\cdot} \end{aligned}\right\}$$

$$\left.\begin{aligned} \sim BO_2^{\cdot} + B &\xrightarrow{k_{BB}} \sim BOOB^{\cdot} \\ \sim BO_2^{\cdot} + A &\xrightarrow{k_{BA}} \sim BOOA^{\cdot} \end{aligned}\right\} \qquad (2)$$

$$\left.\begin{aligned} 2\sim AO_2^{\cdot} &\xrightarrow{k_{OA}} \\ 2BO_2^{\cdot} &\xrightarrow{k_{OB}} \\ AO_2^{\cdot} + BO_2^{\cdot} &\xrightarrow{k_{OAB}} \end{aligned}\right\} \text{non-radical products.} \qquad (6)$$

§ By analogy with polymerisation in the absence of O_2, the term oxidative copolymerisation is applied when two and more monomers are involved in the polymerisation process.

Table 5. The constants for oxidative copolymerisation and co-oxidation of monomers*

Monomers and hydrocarbons	r_A	r_B	Φ	Temp., °C	Refs.
		Styrene (A)			
Butadiene	0.42±0.05	2.2±0.5	—	50	109
Butadiene	0.7±0.2	1.5±0.4	—	30	109
Butadiene	0.3±0.06	2.8±0.3	—	80	109
2,3-Dimethylbutadiene	0.37	2.75	—	50	109
α-Methylstyrene	0.48	2.1	6.2	50	9
α-Methylstyrene	0.9±0.1	1.2±0.1	—	60	110
α-Methylstyrene	1.6	0.71	—	70	111
Methyl methacrylate	7.9±1.0	0.078±0.0002	1.9÷1.1	50	9
Methyl methacrylate	3.6	0.28	0.8	60	112
Methyl methacrylate	9.2	0.09	—	50	113
p-Fluorostyrene	2.72	0.088	—	50	108
p-Fluorostyrene	0.89	0.98	—	50	108
p-Bromostyrene	0.88	0.97	—	50	108
p-Iodostyrene	0.705	0.995	—	50	108
p-Methylstyrene	0.71	1.51	—	50	108
p-Cyanostyrene	1 10	0.50	—	50	108
m-Nitrostyrene	1.24	0.32	—	50	113
p-Nitrostyrene	1.20	0.42	—	50	113
p-Nitrostyrene	1.50	0.22	—	60	114
p-Methoxystyrene	0.55	1 20	—	60	114
p-Methoxystyrene	0.38	2.10	—	50	113
Methyl sorbate	0.32	2.45	—	50	113
Methyl eleostearate	0.33	2.92	—	50	113
Tetralin	2.8±0.5	1.2±0.1	—	60	110
Tetralin	2 9	0.47		70	111
Tetralin	2.1	0.49	4.3	70	115
Tetralin	4.2	0.85	2.5	60	112, 116
Tetralin	2.3±0 3	0.43±0.03		60	117
Cumene	20±2	0.052±0.003		60	117
Cumene	6.5±1	−0.2±0.2	—	60	110
Cumene	13	0.1	10.5	60	112, 116
Cumene	18	0.045	—	70	111
Cyclohexene	1.2	0.15	8.7	60	112, 116
		p-Methoxystyrene (A)			
p-Nitrostyrene	2.3	0.17	—	60	114
		α-Methylstyrene (A)			
Methyl methacrylate	15±2	0.041±0.001	0.9−1.4	50	9
Tetralin	5.7	0.51	—	70	111
Cumene	9.3	0.1	—	70	111
		Butadiene (A)			
Tetralin	3.3±0.5	0.22±0.5	—	50	109
Cumene	23±3	0.03±0.01	—	50	109
s-Butylbenzene	25±10	—	—	50	109
Cyclopentene	1.8±0.5	0.58±0.07	—	50	109
Cyclohexene	4±1	0.10±0.03	—	50	109
Cycloheptene	3.0±0.1	0.38±0.02	—	50	109
Cyclo-octene	8±1	0.10±0.02	—	50	109
		Methyl methacrylate (A)			
Tetralin	0.6	2 9	1.7	60	112
Cumene	1.2	1.6	2.2	60	112
Cyclohexene	0.14	0.52	1.2	60	112

* The reaction was initiated in all cases by azobisisobutyronitrile and was carried out in bulk[9,108,111,112,115-117] or in solution[110,114] at P_{O_2} = 760 mmHg [108,110-112,115-117] or 3100 mmHg.[9]

If one of the system components is a saturated hydrocarbon BH, then oxidative copolymerisation is accompanied by joint oxidation:

$$\sim AO_2^{\cdot} + BH \rightarrow \sim AOOH + B^{\cdot},$$
$$\sim BO_2^{\cdot} + BH \rightarrow \sim BOOH + B^{\cdot}$$

with formation of terminal hydroperoxy-units in the polymer chains or of the hydroperoxide BOOH. It has been shown that the familiar equations for the composition of the copolymer and the general equation for the rate of reaction in three-component systems (the case where one of the monomers is incapable of homopolymerisation) are applicable to the oxidative copolymerisation of two monomers[9,108]. The relative chain propagation rate constants $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$ as well as the ratio of the rate constants for chain termination $\Phi = k_{OAB}(k_{OA}k_{OB})^{1/2}$ can be determined from these equations. The quantity r expresses the selectivity of the peroxy-radicals with respect to the monomers (the ratio of the rates of addtion to its "own" and "foreign" monomers), while the constant Φ represents the difference between the rates of chain termination as a function of the type of reacting peroxy-radicals.

The oxidative copolymerisation and co-oxidation constants for the monomers are listed in Table 5. The small number of publications and the extremely limited number of systems investigated are striking. A comparison of the results obtained by different workers is possibly only for the systems styrene–α-methylstyrene–O_2, styrene–methyl methacrylate–O_2, styrene–tetralin–O_2, and styrene–cumene–O_2. The reason for this is primarily the considerable experimental difficulties associated with a sufficiently accurate determination of the composition of polymeric peroxides, or with the measurement of the concentration of the monomer in the substrate undergoing oxidation[115,117].

Table 6. The chain propagation and termination rate constants for certain vinyl monomers*

R	monomer	$10^3 k_2/k_6^{1/2}$, litre$^{-1/2}$ mole$^{-1/2}$ s$^{-1/2}$ 50° C	$10^3 k_2/k_6^{1/2}$, litre$^{-1/2}$ mole$^{-1/2}$ s$^{-1/2}$ 30° C	k_2, litre mole^{-1} s^{-1} (30°C)	$10^{-7}k_6$, litre mole^{-1} s^{-1} (30°C)
	CH_2 = CHR monomers				
—CH=CH_2	Butadiene	11.9	—	—	—
—C_6H_5	Styrene	13.7	6.3	4.1	4.2
—CN	Acrylonitrile	2.20	0.47	3.3	6.0
—C(O)—CH_3	Methyl vinyl ketone	1.38	—	—	—
—C(O)—OCH_3	Methyl acrylate	0.42	0.14	0.6	1.7
O—C(O)—CH_3	Vinyl acetate	0.61	0.35	2.4	4.9
	$CH_2 = C(CH_3)-R$ monomers				
—CH=CH_2	—	—	—	—	—
—C_6H_5	α-Methylstyrene	23.0	13.0	10	0.06
—CN	Methylacrylonitrile	4.60	1.50	4.5	0.93
—C(O)—CH_3	Isopropenyl methyl ketone	2.22	—	—	—
—C(O)—OCH_3	Methyl methacrylate	1.42	0.48	0.5	0.10
O—C(O)—CH_3	Isopropenyl acetate	0.24	0.16	0.2	0.16

* The Table was set up on the basis of published data for butadiene[109], styrene[46,77], acrylonitrile[56,57], methyl vinyl ketone[46] methyl acrylate[56,65], vinyl acetate[56,66] α-methylstyrene[79], methylacrylonitrile[54,56], isopropenyl methyl ketone[54], methyl methacrylate[39,63], and isopropenyl acetate[54,56].

For all the pairs investigated, if $r_A < 1$ then $r_B > 1$ and, conversely, when $r_A > 1$ then $r_B < 1$ (Table 5), i.e. peroxy-macroradicals react predominantly with one of the monomers. The growing peroxide chains add to the "foreign" monomer ($r_A < 1$, $r_B < 1$) only in the oxidative copolymerisation of styrene with *p*-chloro-, *p*-bromo-, or *p*-iodo-styrene. When the comonomers of styrene and oxygen are compounds having conjugated double bonds (butadiene, 2,3-dimethylbutadiene, methyl sorbate, or methyl eleostearate), or α-methylstyrene, then the peroxy-macroradicals react preferentially with these compounds and

not with styrene. On the other hand, in the system butadiene (styrene)–O_2–tetralin (cumene or other hydrocarbons) the addition of peroxy-radicals is always much faster than the rate at which they abstract hydrogen.

The product $r_A r_B \simeq 1$ in the system styrene-butadiene–O_2, styrene-2,3-dimethylbutadiene–O_2, styrene–α-methylstyrene–O_2, and styrene (butadiene)–hydrocarbon–O_2. The product can serve as a measure of the selectivity of peroxy-radicals, because $k_{AB} = k_{BB}$ and $k_{AA} = k_{BA}$ when $r_A r_B = 1$. In the above systems each monomer exhibits approximately the same reactivity in relation to the radicals $AO_2^{\cdot}$ and $BO_2^{\cdot}$, while the reactivities of peroxy-radicals of both types differ insignificantly and depend little on the structure of their penultimate unit A or B. The absence of selectivity in relation to radicals is responsible for the disordered arrangement of the ~BOO~ and ~AOO~ units in the polyperoxide chains.

IV. RELATION BETWEEN THE STRUCTURE AND REACTIVITY OF MONOMERS[88]

The monosubstituted vinyl monomers investigated, which have the structure $CH_2 = CHR$, can be arranged in the following sequence in terms of increasing $k_2/k_6^{1/2}$: methyl acrylate ≃ vinyl acetate < methyl vinyl kentone < acrylonitrile < styrene < butadiene (series I) (Table 6). The corresponding series II formed by 1,1-disubstituted monomers having the structure $CH_2 = C(CH_3)R$ is: isopropenyl acetate < methyl methacrylate < isopropenyl methyl ketone < methylacrylonitrile < α-methylstyrene (Table 6). The chain propagation rate constants k_2, the absolute values of which exert a decisive influence on $k_2/k_6^{1/2}$, increase in the same sequence.

Table 7. The relative reactivities of the monomers ($1/r$) towards the polymeric radicals ~$MO_2^{\cdot}$ and ~$M^{\cdot}$ *

Monomer	~$MO_2^{\cdot}$ radicals (50°C) from				~$M^{\cdot}$ radicals (60°C) from		
	butadiene	α-methylstyrene	styrene	methyl methacrylate	butadiene	styrene	methyl methacrylate
Butadiene	1.0	—	2.4	—	1.0	—	4.0
α-Methylstyrene	—	1.0	2.1	25	—	0.85	2.0
Styrene	0.46	0.48	1.0	13	0.72	1.0	2.0
Methyl methacrylate	—	0.07	0.13	1.0	—	2.0	1.0

* The Table was set up on the basis of published data for oxidative copolymerisation[9,109,117] and copolymerisation[118].

However, comparison of the values of k_2 yields only a general idea about the efficiency of the elementary addition step for different monomers, since the absolute rate constants depend on the reactivity of both the monomer and the polyperoxy-radical. In order to discover which of the above factors is of decisive importance in oxidative polymerisation, it is necessary to find out how the reactivity of the monomers and the peroxy-radicals varies in the series under consideration. Judging from the form of variation of the reciprocals of the copolymerisation rate constants $1/r$ (Table 7) and the chain propagation rate constants (Tables 4 and 8), the reactivity of monomers as peroxy-radical acceptors increases in the following sequence: methyl methacrylate < styrene < α-methylstyrene < butadiene. For the remaining compounds in series I and II, there is no information about $1/r$ and $k_{AB}(k_{BA})$. This makes it necessary to infer the reactivity of the monomers from the rate of addition of the polymeric radicals ~$M^{\cdot}$ and not ~$MO_2^{\cdot}$, assuming that the monomer activity series do not then change significantly. This assumption may be resorted to on the basis of the concordant results obtained for butadiene, α-methylstyrene, styrene, and methyl methacrylate as regards the rates at which they accept the ~$M^{\cdot}$ and ~$MO_2^{\cdot}$ radicals (Table 7). According to copolymerisation data[118,120], the reactivity of monomers with respect to the radicals ~$M^{\cdot}$ varies in the following way: vinyl acetate < methyl acrylate < acrylonitrile < methyl vinyl ketone < styrene < butadiene (series III) and isopropenyl acetate < methyl methacrylate < methylacrylonitrile < α-methylstyrene (series IV).

According to the available extremely limited data (Table 8), the reactivity of peroxy-radicals ~$MO_2^{\cdot}$ derived from the monomers in reactions involving addition to a double bond decreases in the sequence: styrene > methyl methacrylate > α-methylstyrene. One should also note that secondary peroxy-radicals are more reactive than tertiary radicals not only in the hydrogen abstraction reaction[91], but also in addition to the double bond (Table 8) and in recombination steps (Table 3).

Table 8. The rate constants (litre $mole^{-1}s^{-1}$) of reactions of the ~$MO_2^{\cdot}$ and ~$M^{\cdot}$ polymeric radicals with monomers*

Monomer	~$MO_2^{\cdot}$ radicals (50°C) from			~$M^{\cdot}$ radicals (60°C) from	
	styrene	methyl-metha-crylate	α-methyl-styrene	styrene	methyl-methacrylate
α-Methylstyrene	204	43	28	—	1050
Styrene	98	23	13	170	1050
Methyl methacrylate	12	1.8	1.8	310	520

* The rate constants for the ~$MO_2^{\cdot}$ radicals were calculated from the values of r_A and r_B (Mayo et al.[9]) and from k_2.[63,78,79] Those for the ~$M^{\cdot}$ radicals were calculated from r_A and r_B (Ham[118]) and from k_3.[32,119]

The identical arrangements of the monomers in sequences I and III and II and IV support the conclusion that the main factor in oxidative polymerisation, which determines the overall rate of the process, is the reactivity of the monomers and not peroxy-radicals. This conclusion is consistent with the earlier hypothesis that the activity of the double bond plays a decisive role in oxidative polymerisation[9].

A rigorous justification of the above relation can be achieved at the present time only for α-methylstyrene and methyl methacrylate. ¶ In the oxidative polymerisation of these monomers the increase of $k_2/k_6^{1/2}$ and k_6 on passing

¶ In the oxidative copolymerisation of α-methylstyrene with styrene and of methyl methacrylate with styrene the products are tertiary and secondary peroxy-radicals respectively, having significantly different reactivities, which hinders a rigorous interpretation of the type of variation of $k_2/k_6^{1/2}$ and k_2.

from α-methylstyrene to methyl methacrylate parallels the increased reactivity of the monomers and is in opposition to the decreased reactivity of the radicals.

The increase of the rate of homopolymerisation of vinyl monomers is known to be equal to the increase in the reactivity of the corresponding macroradicals[32]. The inversion of this relation in oxidative polymerisation must be attributed to the nature of the chain-carrier radical resulting from the conversion of ~M· into $MO_2^·$ via the reaction ~M· + O_2 → ~$MO_2^·$. A direct comparison of the reactivities of the polymeric radicals ~M· and ~$MO_2^·$ is at present possible only for styrene and methyl methacrylate, because the required data are lacking for the remaining monomers.

Table 9. The rate constant ratios k_3/k_1 and the rate constants for the reaction ~M· + O_2 $\xrightarrow{k_1}$ ~$MO_2^·$ (at 50°C)*

Radical	Medium	$10^6 k_3/k_1$	k_1, litre mole^{-1} s^{-1}	Refs.
$-CH_2-\dot{C}H-CH=CH_2$	Butadiene	7.0±2.5	$1.0\cdot10^7$	82
$-CH_2-\dot{C}H-C_6H_5$	Styrene	3.7±0.4	$3.3\cdot10^7$	24
	Styrene	1.8	$6.6\cdot10^7$	25
	Styrene-benzene	⩽70	$1.7\cdot10^6$	26
$-CH_2-\dot{C}(CH_3)-C(O)-OCH_3$	Methyl methacrylate	50±3 0	$7.2\cdot10^6$	3
	Methyl methacrylate-benzene	⩽30	$1.2\cdot10^7$	2

* The values of k_3/k_1 were determined[3,24,25,82] from the results of the analysis of the composition of polymeric peroxides. The values of k_3/k_1 were estimated[3,26] from the results of the study of the overall kinetics of the polymerisation reaction. The rate constants k_1 were calculated with k_3 = 70, 120, and 360 litre mole^{-1}s^{-1} for butadiene, styrene, and methyl methacrylate respectively[32].

The peroxy-radical derived from methyl methacrylate is less active in the addition to the double bond than the peroxy-radical derived from styrene, while the opposite relation is observed for the ~M· radicals derived from the same monomers (see Table 8 and Bagdasar'yan's book[32], p.207). The reactivities of the ~M· and ~$MO_2^·$ radicals can be compared directly for each monomer in terms of the chain propagation rate constant ratio k_3/k_2 †. In this case the monomer from which the radicals have been derived serves for them as a comparison standard:

$$\sim M^· + M \xrightarrow{k_3} \sim MM^· \text{ and } \sim MO_2^· + M \xrightarrow{k_2} MO_2M^·.$$

The conversion of the radical ~M· into ~$MO_2^·$ is as a rule associated with a sharp decrease in the reactivity of the radical towards addition to the double bond, the decrease being more pronounced the more reactive was the radical ~M· (Table 10). The validity of this rule for all peroxy-radicals in the monomer series I and II should have the inevitable consequence that the decisive factor in oxidative polymerisation becomes the reactivity of the monomers and not the radicals. The levelling of the reactivities of the radicals on passing from ~M· to ~$MO_2^·$ is most probably caused by the significant decrease in the influence of the structure of the M monomer molecule on the reactivity of a free radical of the type ~$MO_2^·$ compared with a radical of the type M·. This influence does not apparently extend beyond the oxygen atom of the ~$MO^·$ fragement of the ~MOO· unit, because the directions of the orbitals of the lone electron pairs of the oxygen atoms in the -O-O- peroxy-groups are mutually perpendicular[121]. This is probably also the cause of the comparatively small change in the reactivity of primary, secondary, and tertiary radicals $RO_2^·$ in the abstraction of hydrogen atoms as a function of the structure of R [91,122,123] (Table 4).

† k_3/k_2 can be estimated from the ratio $k_3/k_4^{1/2} : k_2/k_6^{1/2}$, because $k_4^{1/2} = k_6^{1/2}$ (to within an order of magnitude).

Table 10. The rate constants for the polymerisation and oxidative polymerisation reactions of certain monomers (at 50°C)*

Monomer	$10^3 k_6/k_6^{1/2}$, litre mole^{-1} s^{-1}	$10^3 k_3/k_4^{1/2}$, litre mole^{-1} s^{-1}	γ	k_2, litre mole^{-1} s^{-1}	k_3, litre mole^{-1} s^{-1}	γ'
Styrene	13.7	15.0	1.1	98	120	1.2
Acrylonitrile	2.20	61.0	28	—	—	—
Methyl methacrylate	1.42	79.3	56	1.8	360	200
Vinyl acetate	0.61	264	430	—	—	—
Methyl acrylate	0.43	510	1200	1.7	980	570

* The values of $k_2/k_6^{1/2}$ and k_2 were obtained from the published data for styrene[46,77], acrylonitrile[56], methyl methacrylate[81,82], vinyl acetate[57,66], and methyl acrylate[57,65]. The values of $k_3/k_4^{1/2}$ and k_3 were evaluated from data of Bagdasar'yan[32]. Notation: $\gamma = k_3/k_4^{1/2} : k_2/k_6^{1/2}$; $\gamma' = k_3/k_2$.

The arrangement of the monomers in series I and II shows that the influence of substituents in these compounds on their reactivity decreases in the sequence $-CH_2=CH_2 \simeq C_6H_5- > -CN > -C(O)-CH_3 > -C(O)-OCH_3 \simeq OC(O)-CH_3$. In radical addition reactions of the same type the influence of substituents is interpreted on the hypothesis of a linear relation between the change in activation energy and the conjugation energy in the reacting molecules and radicals[32,124]. This approach is also possible in oxidative polymerisation. Allowance for other factors (apart from conjugation) capable of influencing the radical reactivity is at the present time still fairly difficult[125,126]. The treatment of the reactivities of monomers in oxidative polymerisation from the standpoint of the influences which the substituents exert on the electron density in π bonds is also acceptable. Calculations of the distribution of electron density in monomers[127,128] showed that the π-electron density in double bonds decreases in the sequence styrene > acrylonitrile > methyl methacrylate > methyl acrylate > vinyl acetate. Thus there is a correspondence between the change in the reactivity of the monomers in oxidative polymerisation and the electron density in their π bonds. This feature is consistent with the electron-accepting properties of peroxy-radicals[9,129].

Judging from the values of $k_2/k_6^{1/2}$ and k_2, unsaturated 1,1-disubstituted compounds having the structure $CH_2 = C(CH_3)R$ as a rule interact with oxygen at higher rates than the corresponding monosubstituted compounds $CH_2 = CHR$ (Table 6). The decrease of k_6 from 3×10^7 litre mole^{-1}s^{-1} to 7×10^5 litre mole^{-1}s^{-1} (at 50°C) makes a significant contribution to the increase of the ratio $k_2/k_6^{1/2}$ for α-methylstyrene relative to styrene, which compensates the

decrease of k_2 (Tables 2 and 3). However, the introduction of a more bulky substituent in the α-position relative to the double bond (for example in α-phenylstyrene) also leads to a decrease of $k_2/k_6^{1/2}$ (Table 2). The introduction of an electron-accepting substituent in the β-position reduces sharply the rate of oxidative polymerisation: β-bromostyrene reacts with oxygen at a rate smaller by two orders of magnitude than styrene or β-methylstyrene (Table 2). The introduction of electron-donating substituents (CH_3, CH_3O, etc.) in the *para*-position in the styrene ring increases the reactivity of the monomers, while electron-accepting substituents (F, NO_2) reduce it significantly (Table 5).

The rate of oxidative polymerisation of α-substituted derivatives of acrylonitrile varies as follows: methylacrylonitrile > ethylacrylonitrile > n-propylacrylonitrile > isopropylacrylonitrile > n-pentylacrylonitrile (Table 2). The hyperconjugation effect, arising owing to the interaction of the σ electrons of the C–H bonds of the substituents with the π electrons of the $H_2C = C(R)-C \equiv N$ conjugated system, probably increases in the above sequence, lowering the electron density in the double bond.

It has been established[46,63] that the quantity $k_2/k_6^{1/2}$ and correspondingly the rates of interaction of monomeric methacrylates and acrylates with oxygen, as well as the chain propagation rate constants k_2 depend only slightly on the size of the substituent R in the alkoxy-group in the esters $CH_2 = C(R_1)C(O)OR$, where R_1 = H or CH_3 and R = CH_3, C_4H_9, C_9H_{19}, or $C_{16}H_{33}$ (Tables 2 and 3). It is most likely that the substituent R has no significant influence on the reactivity of the double bonds in the peroxy-radicals of acrylates and methacrylates. The double bonds in methacrylate esters are more reactive than those in acrylate esters in the addition reactions of both M$^{\cdot}$ [32] and $RO_2^{\cdot}$ [46] radicals. Presumably secondary peroxy-radicals having the structure $-CH_2-CH(R)(O)O^{\cdot}$ are more reactive than the tertiary radicals $-CH_2-C(R)(CH_3)OO^{\cdot}$ not only in the recombination reaction (Table 6) but also in the addition reaction. The opposite variation of the reactivities of the double bonds and free radicals should lead to the mutual approach of the values of k_2 for acrylates and methacrylates.

V. OXYGEN AS AN INHIBITOR OF RADICAL POLYMERISATION[88]

Oxygen is known to be an inhibitor of the polymerisation of vinyl monomers[2,32,130]. Saturation of the monomers with oxygen (air) reduces the rate of polymerisation and leads to the appearance of an inductive period. Inhibition takes place as a result of the highly efficient chain transfer of oxygen via the raction $\sim M^{\cdot} + O_2 \longrightarrow MO_2^{\cdot}$ and slow regeneration of the chain by peroxy-radicals: $\sim MO_2^{\cdot} + M \longrightarrow \sim MO_2M^{\cdot}$, because the rate of addition of the radical $\sim MO_2^{\cdot}$ to the double bond is much smaller than the rate of chain propagation: $\sim M^{\cdot} + M \longrightarrow \sim MM^{\cdot}$.

The available data make it possible to consider the mechanism of the inhibiton process and to observe the relation between the reactivity of monomers and the efficiency of the action of oxygen on radical-chain polymerisation.

Oxygen combines very rapidly with free radicals having an unpaired electron on a carbon atom, which serve as chain carriers in radical-chain polymerisation. The values of k_1 for the radicals M$^{\cdot}$ derived from butadiene, styrene, and methyl methacrylate lie in the range 2×10^6 – 7×10^7 litre mole^{-1}s^{-1} (at 50° C) and depend little on the structure of the radical (Table 9). In general, the characteristic values of the rate constants k_1 for the reaction $R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot}$ are 10^6–10^8 litre mole^{-1}s^{-1}.[119] Judging from the values of k_1 quoted, oxygen reacts with free radicals of the type $R_1R_2R_3C^{\cdot}$ at the same rate as a free radical (typical values of k_4 and k_6 for the recombination reaction $2 \sim M^{\cdot} \xrightarrow{k_4}$ and $2RO_2^{\cdot} \xrightarrow{k_6}$ are 10^6–10^7 litre mole^{-1}s^{-1} [32,119]). This behaviour of oxygen can be accounted for by the characteristics of the electronic structure of its molecule. Oxygen in its ground electronic state is a biradical which has a $\sigma-\pi-\pi$ bonding skeleton and in addition two electrons with parallel spins in antibonding molecular orbitals.[131,132]

The ratio of the rates of the competing chain propagation reactions $\sim M^{\cdot} + M \xrightarrow{k_3} \sim MM^{\cdot}$ and the chain transfer to oxygen $\sim M^{\cdot} + O_2 \xrightarrow{k_3} \sim MO_2$ is given by the expression $W_3/W_i = k_3[M]/k_1[O_2] = \alpha$. Using α as a criterion, it is possible to estimate the probability of non-inhibited polymerisation steps in the presence of oxygen. According to estimates, the reaction $\sim M^{\cdot} + M \rightarrow \sim M^{\cdot}$ is suppressed in the temperature range 20–60° C for all vinyl monomers, including vinyl acetate and methyl acrylate which generate the most reactive radicals under the conditions of saturation with oxygen (according to the data in Table 10, the values of α for butadiene, styrene, and methyl methacrylate are 2.8×10^{-3}, 4.4×10^{-3}, and 5×10^{-2} respectively at 50° C).

Thus, during the induction period, the monomer and oxygen react in equimolar proportions via the mechanism represented by the elementary reactions (0), (1), (2), and (6) in Scheme 1; the rate of consumption of oxygen is constant and the reaction is of zero order with respect to O_2. The kinetics of polymerisation inhibited by oxygen[2,26,133] and also by oxygen and antioxidants present simultaneously[134–139] have been examined in detail. The range of oxygen concentrations in which O_2 exerts the maximum inhibiting effect on the polymerisation of monomers is defined by the relation $[O_2] \geqslant k_3[M]/0.1k_1$. Only at the end of the induction period does the O_2 concentration fall to values such that α proves to be greater than 0.1 and the $\sim MO_2^{\cdot} + \sim M^{\cdot}$ chain cross-termination reaction and the $\sim M^{\cdot} + M \rightarrow \sim MM^{\cdot}$ homopolymerisation steps become insignificant.

Since the efficiency of chain transfer to oxygen is extremely high, the $\sim M^{\cdot} + M \rightarrow \sim MM^{\cdot}$ chain propagation steps take place with a very low probability and the only pathway involving the consumption of the monomer becomes the chain regeneration reaction. The kinetic effect of oxygen on the polymerisation of the monomer is therefore determined by the ratio of the rate of chain propagation W_3 in the absence of O_2 to the rate of chain regeneration W_2, where $W_3 = (k_3/k_4^{1/2})[M]W_i^{1/2}$ for $P_{O_2} = 0$ and $W_2 = (k_2/k_6^{1/2}) \cdot [M]W_i^{1/2}$ when peroxy-radicals are responsible for chain termination: $2MO_2^{\cdot} \rightarrow$ chain termination. When the rates of initiation are equal, we obtain $W_3/W_2 = k_3k_6^{1/2}/k_4^{1/2}k_2 \cdot k_3/k_4^{1/2}$ and $k_2/k_6^{1/2}$ vary in opposite senses (Table 10) in the series styrene, acrylonitrile, methyl methacrylate, vinyl acetate, and methyl acrylate, in full agreement with the fact that k_3 is determined by the reactivity of the radical (homopolymerisation) and k_2 is determined by the reactivity of the monomer (oxidative polymerisation). In the above series of compounds the ratio W_3/W_2 increases sharply by three orders of magnitude, the inhibition of polymerisation being more pronounced the less reactive the monomer. This behaviour is a consequence of the decisive role of the reactivity of monomers in oxidative

polymerisation. Increasing inhibition of polymerisation is inevitable when the relatively unreactive peroxy-radicals interact with increasingly less reactive monomers. In homopolymerisation, where the reactivities of the monomers and radicals vary in opposition, the low reactivity of the monomer is swamped by the high reactivity of the radical[32].

Thus the efficiency of the inhibiting effect of oxygen varies in opposition to the reactivity of the monomer in the polymerisation reaction. This behaviour makes it possible to predict the influence of oxygen on radical polymerisation from the available literature values of $k_3/k_4^{1/2}$ and k_3, having adopted styrene as the reference monomer (since $W_3/W_2 \simeq 1$ for this compound in the temperature range 20–70°C).

* * *

It follows from the data presented that the fundamental elementary reactions in the oxidative polymerisation of vinyl monomers have now been established. The mechanism of the oxidative polymerisation of styrene, α-methylstyrene, methyl methacrylate, and butadiene has been studied comparatively fully. The kinetics of the interaction with oxygen of a series of other monomers have also been investigated, but the available information about the rate constants for the elementary reactions remains extremely limited. The results obtained made it possible to determine the nature of the relation between the structure of a vinyl monomer and its reactivity in oxidative polymerisation, and to discover the characteristics of the behaviour of oxygen as an inhibitor of radical-chain polymerisation. In general, oxidative polymerisation, which represents the boundary between radical-chain polymerisation and oxidation, has still been clearly inadequately investigated. A marked deficiency of data on the chemistry, kinetics, and thermodynamics of the interaction of oxygen with unsaturated compounds is felt. The most urgent task is a quantitative investigation of the mechanism of the oxidative polymerisation of vinyl monomers at advanced stages of the reaction, particularly in highly viscous media, including reactions in the solid phase. In combination with the study of macroscopic process kinetics, further studies on these lines will make it possible to lay the theoretical foundations for the formation of films of unsaturated compounds and will permit an expansion of research on the stabilisation of organic protective coatings.

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