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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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To cite this Article Kishore, K. , Gayathri, V. and Ravindran, K.(1981) 'Formation and Degradation of Polymeric Peroxides', Journal of Macromolecular Science, Part A, 16: 8, 1359 — 1383
To link to this Article: DOI: 10.1080/00222338108063242
URL: http://dx.doi.org/10.1080/00222338108063242

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J. MACROMOL. SCI.–CHEM., A16(8), pp. 1359-1383 (1981)

Formation and Degradation of Polymeric Peroxides

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ABSTRACT

An attempt has been made to bring the literature on polymeric peroxides together from all angles in order to present a comprehensive picture about them. Both polyperoxides, where the peroxide group has been attached to the main chain, and polymeric hydroperoxides, where the peroxide group is present as a side chain, have been considered. Various aspects such as formation, thermal decomposition characteristics, photodecomposition, and analysis of peroxides have been discussed.

INTRODUCTION

Organic peroxides are one of the important classes of compounds in chemistry. They are important both from the point of view of understanding the mechanism of oxidation of organic compounds and for the synthesis of polymers. They can be broadly classified into polymeric and nonpolymeric peroxides. An attempt was made to review the polymeric peroxides in 1968 [1]. No recent review is available although a lot of literature has been collected since then. Moreover, in this particular review, only the peroxides of styrene, butadiene, and indene were discussed briefly. In the present review, literature on various aspects such as formation, degradation, and

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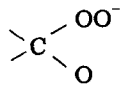
TABLE 1

Peroxide class	General structure[a]
Peroxides	ROOR
Hydroperoxides	ROOH
α-Oxy and α-peroxy hydroperoxides and peroxides	
Peroxy acids	$R(CO_3H)_n$
Diacyl peroxides	$RC(O)OOC(O)R^1$
Peroxy esters	$R[(CO)_3R^1]_n$

[a]R and R^1 represent hydrocarbons.

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analysis of polymeric peroxides has been brought together in order to present a comprehensive picture of polymeric peroxide.

Before discussing the polymeric peroxides, it is worthwhile to discuss briefly important information regarding nonpolymeric peroxides. Nonpolymeric peroxides can be generally classified into the categories listed in Table 1.

Oxygen is the primary source of the –O–O– linkage in organic peroxides, whether they are prepared by direct air oxidation or by the reaction of organic compounds with peroxide material or ozone.

The general methods of preparation are:

1. By the reaction of organic compounds with H_2O_2 or alkyl peroxides
2. By the autoxidation of organic compounds
3. By the reaction of organic compounds with ozone
4. Miscellaneous methods, where hydroperoxide can be obtained by the hydrolysis of alkyl peroxides etc.

The literature on the formation, decomposition characteristics, and analysis of various types of peroxides has been reviewed [2-4].

Polymeric peroxide can be classified into the following two categories:

1. Polyperoxides where the peroxy group is introduced into the main chain, giving rise to polymeric peroxides of the type ROOR, generally formed by the copolymerization of oxygen and monomer composing the largest group of polyperoxides.
2. Polymeric hydroperoxide in which the O_2 is included in the polymer as a side chain, usually formed by the oxidation of polymers.

FORMATION OF POLYMERIC PEROXIDES

Polyperoxides

In polyperoxides of the type ROOR, formed by adequate amounts of O_2, the peroxide (–O_2–) and monomer (–M–) units alternate giving the formula $(MO_2)_x$, where x is the degree of polymerization. In the absence of insufficient oxygen, less oxygen is incorporated and the formula becomes $(M_yO_2)_x$ where $y > 1$. The reaction is free radical in nature and the reaction mechanism for the formation of polyperoxide is as follows:

Initiation

$$\text{Initiator} \longrightarrow 2I^{\bullet} \tag{1}$$

$$I^{\bullet} + O_2 \longrightarrow IO_2^{\bullet} \tag{2}$$

Propagation

$$IO_2^{\bullet}\ (PMO_2^{\bullet}) + M \longrightarrow IO_2M^{\bullet} \text{ or } PMO_2M^{\bullet} \tag{3}$$

$$PM^{\bullet} + O_2 \longrightarrow PMO_2^{\bullet} \tag{4}$$

$$PM^{\bullet} + M \longrightarrow PMM^{\bullet} \tag{5}$$

$PM^{\bullet}$ and $PMO_2^{\bullet}$ are the polymer radicals ending with monomer and O_2 units, respectively.

Termination

$$\left.\begin{array}{l} 2PMO^{\bullet} \quad (6) \\ 2M^{\bullet} \quad (7) \\ PM^{\bullet} + PMO_2 \quad (8) \end{array}\right\} \longrightarrow \text{nonradical products}$$

If the O_2 concentration corresponds to a pressure of about 100 torr, Reaction (4) is much faster than Reactions (5), (7), and (8), and an alternating 1:1 copolymer is formed. As the O_2 pressure decreases, Reaction (4) becomes slower and Reactions (5), (7), and (8)

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become important. The product contains more M units than peroxide units.

A survey of polymeric peroxides, principally those of styrene, α-methylstyrene, indene, and butadiene, has been made by Dale [1]. Formation mechanism, structure, and polymer reactions are discussed.

Peroxide of Styrene and Substituted Styrene

The oxidation of unsaturated compounds has been studied, particularly the oxidation of styrene, in great detail, by Mayo et al. [5-13]. The rates and products of oxidation of styrene have been studied in the presence and absence of α,α'-azodiisobutyronitrile (ADBN) at 0.1 to 4 atm of oxygen and at 35-85°C. The products of oxidation are polymeric peroxide, benzaldehyde, and formaldehyde. An 18% conversion to polyperoxide was obtained by stirring a 0.02 M solution of ADBN in styrene at 50°C for 24 h under an atmosphere of oxygen and precipitating the polymer with methanol.

The rates and products of oxidation of α-methylstyrene have been studied [12] in the presence of 0.01 M ADBN at oxygen pressures from 0-3200 mm. The primary products are a polymeric peroxide, acetophenone, formaldehyde, and α-methylstyrene oxide. At 50°C the maximum yield of polyperoxide was 83% at 3200 mm pressure of oxygen, 70% at 50-100 mm, and 40% at 6 mm. The effect of oxygen on the oxidation of styrene has been studied [10] at oxygen pressures ranging from 0-3200 mm in the presence of 0.01 M 2,2'-azobis-(2-methyl propionate). In the absence of oxygen, styrene is converted to polystyrene at the rate of 0.095 mol/L·h. Above 10 mm pressure, styrene reacts at a nearly constant rate of 0.06 mol/L·h and the product is mostly poly(styrene peroxide). The rate of reaction of styrene passes through a minimum of 0.03 mol/L·h at about 0.05 mm pressure of oxygen. The O_2:C_8H_8 ratio increases from zero to nearly unity as the oxygen pressure increases from 0 to 100 mm. The effect of structure on the rates and products of oxidation of unsaturated compounds has also been studied [9].

Poly(styrene peroxide) formed during the polymerization of styrene which was previously irradiated with x-rays in the presence of atmospheric oxygen was investigated by Korshak et al. [14]. By irradiation at -5 to 50°C while passing O_2 through styrene, polyperoxides of styrene were formed, which acted as an initiator in the subsequent polymerization of styrene.

Mayo et al. [8, 12] have studied the effects of increasing temperature and rate of oxidation on the formation of the peroxide of α-methylstyrene. They observed that the increase in reaction temperature and rate of oxidation results in lower effective oxygen concentration, increasing the ratio of methylstyrene oxide to acetophenone, rapidly decreasing the formation of polyperoxides above 100°C.

The autoxidation of styrene and substituted styrene was studied by Dulong et al. [15]. Styrene and substituted styrenes were polymerized in the presence of azobisisobutyronitrile and less than 5 mol%

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of oxygen. The peroxide copolymers were isolated, the reactivity of which differed with different para substituents.

Methyl Methacrylate Peroxide

The peroxide of methyl methacrylate was prepared by Pingchang and Tien [16] by passing oxygen into methyl methacrylate at a rate of 2-4 L/h at 40°C in the absence of an initiator. The benzene solution was passed through an alumina column and eluted with 1:4 ethyl alcohol-benzene solution to obtain viscous polymeric peroxide. It was found that the methyl methacrylate peroxide initiated by the polymerization of methyl methacrylate produced a polymer of high molecular weight. The oxidation of methacrylate ester was also studied by Mayo and Miller [17]. The peroxide of methacrylate ester was prepared in a manner similar to that of the peroxide of styrene by the same authors.

Kinetic investigations into the formation of polymeric peroxides of methyl methacrylate were carried out by Kerber [18]. The effect of molecular oxygen in the presence of the radical producing initiators and the effect of the dielectric constant of the solvent used were also determined.

Miscellaneous Peroxides

The liquid phase oxidation of butadiene to poly(butadiene peroxide) $(C_4H_6O_2)_n$ has been investigated to determine the effect of temperature, solvents, oxygen pressure, and catalysts on the rate of formation and structure of the product [19]. Polymeric peroxides of conjugated diolefines were prepared by Hutchinson [20] by treating with O_2 in the presence of an initiator and a catalyst between 71-150°C.

Cellulose acetate peroxide formation was studied by Chodak and Suta [21]. Their results show the degree of acetylation to have the greatest influence on peroxide formation. In the range of 20-40°C there is a linear correlation between peroxide formation rate and temperature. Destruction of peroxides occurs at higher temperatures. The influence of such variables as oxidation time, degree of acetylation, ozone flow rate, and the amount of cellulose acetate were evaluated. The polymeric peroxide of methyl atropate has been prepared by Craig and Tyrrall [22] by allowing methyl atropate to stand in air and then distilling in vacuum to give a 1:1 copolymer of methyl atropate and oxygen, which softens at 85-90°C and then decomposes explosively.

Polymeric peroxides based on copolymers of styrene and p-formylstyrene were prepared by Bylina et al. [23]. PS containing diacylperoxide groups were obtained by oxidation of styrene formyl-styrene copolymer with O_2 in benzene at 40°C. For example:

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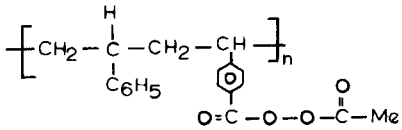

Razuvaev and Minisker [24] have prepared polymeric peroxides of vinyl chlorides by shaking vinyl chloride in air-filled ampules at 50° C for 12 h followed by distillation of monomer. A residue of polymeric vinyl chloride peroxide, a very unstable, yellowish, viscous liquid, was obtained which was handled only in small quantities owing to its explosive character. The polymer of vinyl chloride initiated by vinyl chloride peroxide had a low molecular weight and was more readily decomposed by heat. Its structure probably included units of polyperoxide terminal units.

Polymeric Hydroperoxide

The oxidation of polymers usually yields polymeric hydroperoxides in which O_2 is included in the polymer as a side chain. The hydroperoxides are formed by the reaction of the most labile hydrogen atom in the system; in an unsaturated compound this hydrogen atom is the α-hydrogen atom. The hydroperoxides are usually formed as intermediates in the overall oxidation process and can readily decompose further to give secondary products.

The basic work on the hydroperoxidation mechanism has been adequately reviewed [25]. In brief, it has been established that a radical chain reaction having the following mechanism is involved:

Initiation

Production of radical $R^{\bullet}$

Propagation

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \tag{9}$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \tag{10}$$

Termination

$$\left.\begin{array}{l} R^{\bullet} + R^{\bullet} \\ ROO^{\bullet} + R^{\bullet} \\ RO_2^{\bullet} + RO_2^{\bullet} \end{array}\right\} \longrightarrow \text{nonradical products} \tag{11}$$

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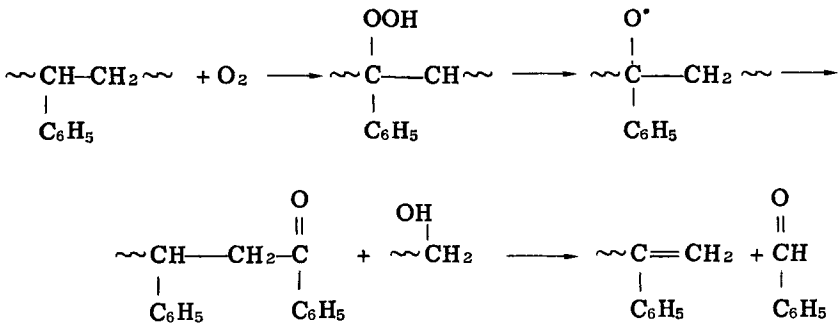
where RH and ROOH represent the compound being oxidized and the resulting hydroperoxide, respectively. The hydroperoxides formed are themselves capable of decomposing to form initiating radicals, so that as the reaction proceeds, the rate accelerates. The primary hydroperoxidation process is masked by hydroperoxide decomposition reactions. It is also autocatalytic and accelerated by light, radical catalysts, and metal ions. Competitive reactions of hydroperoxide formation and decomposition occur throughout the reaction, and the maximum concentration is reached when the rate of decomposition equals that of formation.

Vendenberg [26] has studied the formation of polymeric hydroperoxide and reported that the compound results from liquid-phase oxidation of a polymer containing a cyclic nucleus and an oxidizable hydrogen atom attached to the cyclic nucleus, with free oxygen. He found the hydrogen atom attached to the tertiary carbon atom to be the most easily oxidizable. He has also prepared the PS hydroperoxide by bubbling oxygen into a 1% solution of PS in benzene to which cumene hydroperoxide was previously added. Hydroperoxide was recovered by precipitation with methanol. The site of the radical attack has been established by comparing the oxidation behavior of deutero styrene with that of polystyrene by Wall et al. [27]. Oxidative degradation of a series of deuterated styrene polymers was also studied in the presence of UV irradiation and in air at 60°C [28]. They found that all polymers in which the α-position was occupied by deuterium or a methyl group showed a slower increase in absorbance at 340 mμ as compared to polymers with hydrogen atom in the α-position. Chapiro [29] has reported that during the γ-ray irradiated peroxidation of polymers in air, hydroperoxides were formed above the glass transition temperature and chain peroxide formation was favored below this temperature.

Thermoxidative degradation of PS has been studied by Jellinek [30-33] at 180-280°C in air and the following mechanism has been proposed.



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The sequence has been confirmed by spectrometric techniques such as UV and IR which showed the presence of –C=O and –OH end groups.

Polymeric hydroperoxides have been reported to be formed during photooxidation [34-36]. Irradiation causes the fission of C–H bonds in the polymer with the production of hydrogen atoms as well as hydrocarbon free radicals. Oxygen, because of its radical properties, immediately combines with these radicals. The peroxy radicals thus formed can abstract hydrogen atoms from other parts of the polymer molecule, thus forming hydroperoxide. Photolysis of these peroxide radicals further propagates the oxidation reaction.

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet} \tag{12}$$

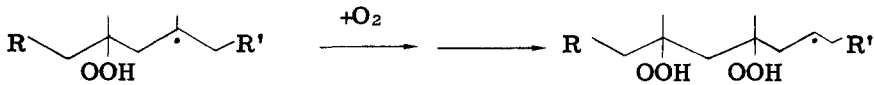
$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \tag{13}$$

$$RO_2^{\bullet} + HR \longrightarrow ROOH + R^{\bullet} \tag{14}$$

$$R^{\bullet} + HOO^{\bullet} \longrightarrow ROOH \tag{15}$$

Even though the polymer does not absorb UV in the longer wavelength region, small quantities of impurities present may absorb these radiations and decompose themselves giving rise to free radicals which initiate oxidation [37]. Small quantities of hydroperoxides which are present in the polymer (due to the mild oxidation during processing) also may decompose by light and thus promote further oxidation. In the case of polypropylane, sequences of hydroperoxides are formed in addition to isolated hydroperoxides in the intramolecular chain oxidations as follows:

(16)



(17)

After a brief exposure to light, considerable quantities of hydroperoxides may be formed and further decomposition is then determined exclusively by their disintegration reactions.

To establish the site of radical attack, the oxidation of polystyrene and a series of polymers prepared from specifically deuterated styrene monomer were investigated in the presence of UV irradiation and

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in air at 60°C. All polymers in which the α-position was occupied by deuterium or a methyl group showed a slower rate of increase in absorbance at 340 mμ [38].

Oxidative degradation of PS and deutero polystyrene in the presence of oxygen at 175-235°C and in the presence of ozone between 65 and 154°C has been studied by Beachell and Nemphol [39]. The products of the reaction analyzed by IR appear to be low molecular weight polystyrene containing carbonyl group upon oxidation, while a peroxide complex intermediate formed primarily during ozonization.

Mass spectrometric experiments by Achhammer and co-workers [40] show the products of polystyrene oxidation to be benzaldehyde, formaldehyde, formic acid, CO, CO_2, and H_2O. All of these are compatible with the decomposition of α-phenyl hydroperoxide. Further, they have confirmed the attack of oxygen at the t-hydrogen atom as is evident by the fact that deuteration at the t-position depressed the rate of oxidation. In spite of all these evidences, it was not possible for them to detect hydroperoxide by the usual analytical methods. This may be due to its instability, the low concentration expected, and the polymer chain environment in which they were analyzed.

During the oxidative degradation of 2% polystyrene solution in CCl_4 at 55°C, Beachell and Smiley [41] were able to identify the presence of peroxides, the concentration of which was found to be about four polymeric peroxide units for every 1000 styrene units. Only the carbonyl group was identified in other cases where polystyrene was oxidized thermally at 200°C for 24 h and polystyrene irradiated at 60°C for periods up to 480 h.

Kinetics of the low temperature reaction $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ in rigid polystyrene and its molecular weight analog were examined [42]. These studies indicated that reaction kinetics depend on different solubility and mobility of oxygen in different segments of the polymer matrix which caused heterogenity in the formation of the peroxide radical.

Detailed studies on the thermal oxidation of polyolefins were carried out by Iring et al. [43-48]. The formation, characterization, and decomposition of polyethylene hydroperoxide were studied [43]. Changes in the molecular weight distribution, weight average molecular weight, and average number of chain scission in the thermal oxidation of low density polyethylene in the melt phase and isotactic polypropylene in the solid phase were determined [44]. They have also studied [45] the overall kinetics of thermal oxidation of high density polyethylene. In the oxidation of 20 μm films of high density polyethylene at 157/650 mm oxygen uptake, weight increases and hydroperoxide formation start with a rate different from oxygen uptake, while rate of formation of carbonyl groups and volatile formation is essentially the same as that of the rate of oxygen uptake. The kinetics of oxygen absorption and weight change as a function of layer thickness was studied for molten polyethylene [46] at 157°C and 650 torr oxygen pressure.

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Zolotova and Denisov [49] have prepared the polyethylene hydroperoxide by oxidizing polyethylene and ethyl methyl ketone peroxide in 1:1 phenyl chloride solution.

THERMAL DECOMPOSITION OF POLYMERIC PEROXIDES

Polyperoxides

Polyperoxides are either colorless oils or crystalline solids, and they sometimes have a yellow color due to partial decomposition. They are generally soluble in aromatic hydrocarbon solvents but insoluble in polar solvent such as alcohol. Most of the peroxides are relatively soluble in the parent monomer, but the polyperoxide of butadiene is not. This insolubility adds to its danger, since once it is formed, even in very low concentrations, it becomes concentrated by separating out.

Like all peroxides, polymeric peroxides decompose fairly readily. A common method of comparing the sensitivity of explosion is the drop-weight test. The pure 1:1 polybutadiene peroxide is considered potentially more sensitive than even TNT. Polyperoxides formed with insufficient oxygen show a reduced sensitivity to shock. Therefore, limiting the oxygen concentration produces a less sensitive polyperoxide.

Miller and Mayo [50] have studied the decomposition of polymeric vinyl peroxides. They report that carbonyl compounds are produced by the thermal oxidation of vinyl peroxides without the reaction between the decomposition products and the peroxide. In their studies, peroxides were decomposed by adding dropwise a solution of peroxide in benzene to a flask kept at 260-280°C in a nitrogen stream. The product was condensed and found to be benzaldehyde and some formaldehyde.

Tsvetkov and Markovskaya [51] have studied the decomposition of aliphatic dicarboxylic polymeric peroxides in solution. A kinetic equation of the reaction of thermal decomposition of the polymeric peroxide of dicarboxylic aliphatic acids was established and proved. Decomposition of polymeric peroxide proceeds by an intramolecular process, particularly at increased temperature and decreased distance between the peroxide bonds in the polymer chain.

Decomposition of polystyrene peroxide has been studied in great detail and a mechanism has been proposed by Mayo and Miller [6]. The principal reaction of styrene peroxide is the cleavage of a peroxide bond into two alkoxy radicals initiated by heat or light. These radicals then alternately lose benzaldehyde and formaldehyde units in an exothermic chain reaction. Another important reaction of styrene peroxide involves the rearrangement of hydrogen atoms among units in a peroxide chain. The transfer may occur by a radical or nonradical mechanism:

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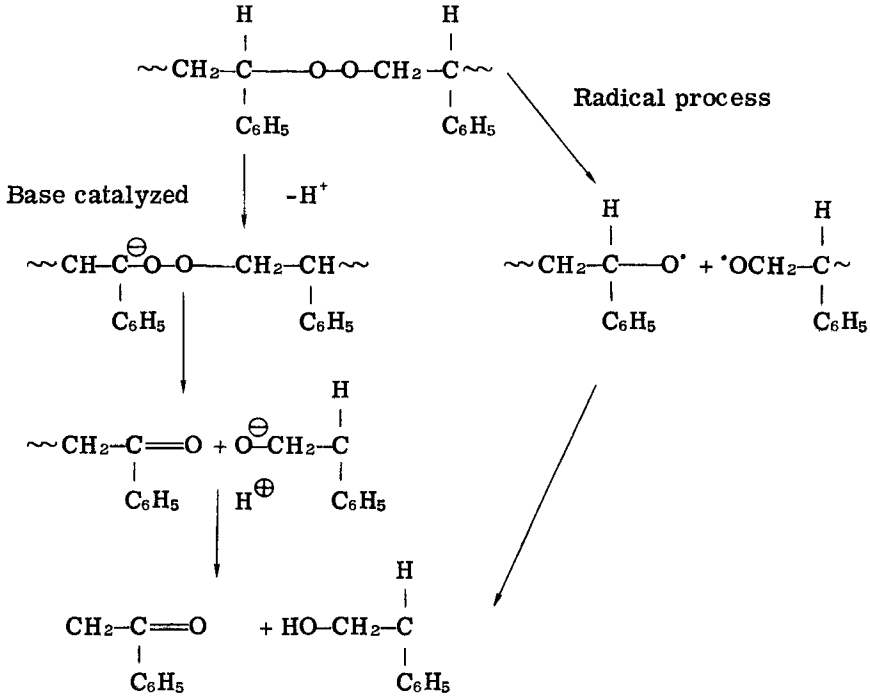

Under the influence of heat or light, styrene peroxide decomposes principally by the chain mechanism to give benzaldehyde and formaldehyde. The decomposition may become explosive above 110°C.

Recently in our laboratory some studies have been carried out on the kinetics of thermal decomposition of polystyrene peroxide [52]. The activation energy for decomposition was found to be 30 kcal/mol employing both the Jacobs-Kureishy's equation and the first-order kinetic equation. This suggests that the rate controlling step of decomposition is breakage of the O–O bond. The experimentally determined heat of decomposition (ΔH) value tallied fairly well with the calculated value (calculated for the decomposition of polystyrene peroxide to benzaldehyde and formaldehyde), showing once again the breakage of the O–O bond to be the rate controlling step. Kishore [53] reported that during the decomposition of poly(styrene peroxide), the order of the reaction changes with temperature. The order of the reaction was obtained from the DSC data using

$$S/\Delta H = (1 - \alpha)^n A e^{-E/RT} \tag{18}$$

where S is the DSC signal in millicalories per second for full-scale deflection, ΔH is the total heat of PSP decomposition, A is the frequency factor, and R is the gas constant. n values were calculated

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from the slope of the plot of ln (S/ΔH) vs ln (1 - α). It was found that n is 2 at 405 K, 1.8 at 410 K, and 1.2 at 415 K. Thus, as the reaction proceeds, n decreases from 2 to 1. Since the E value remains constant throughout the reaction region, the observed change in the n value suggests that although the rate controlling step is the dissociation of the O–O linkage, the actual mode of dissociation changes during the course of decomposition.

Kinetics and thermal decomposition of polymeric peroxides of pimelic acid, azelaic acid, and sebacic acid depend on the thermodynamic quality of the solvent, concentration of the peroxide, and extent of reaction [54]. A correlation has been established between the decomposition mechanism and the concentration of the polymeric peroxide. The correlation has been explained by changes in the conformation of the latter. A mathematical treatment of the kinetics of thermal decomposition of polymeric peroxides in solution is presented by Tsvetkov and Markovskaya [55].

The formation of benzaldehyde, the main intermediate during the oxidation of styrene at 70°C and 760 mmHg, was investigated [56] by Dutka and Gal using a kinetic isotope method by adding ^{14}C labeled benzaldehyde to the system. The rate of formation of benzaldehyde was found to be much larger than of its further oxidation. Carbonyl compounds produced by the thermal decomposition of vinyl peroxides were studied by Miller and Mayo [57], without the danger of explosion and without the reaction between the decomposition products and the polymeric peroxide. Polystyrene peroxide was prepared as described earlier [5], and it decomposed instantly upon contact with a hot surface under inert atmosphere. The condensed products yielded benzaldehyde and formaldehyde.

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Polymeric Hydroperoxides

Homolytic cleavage of the O–O bond generally occurs, when peroxides are decomposed thermally or by irradiation:

$$\mathrm{ROOH} \xrightarrow{\Delta/h\nu} \mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OH} \tag{19}$$

The ultimate fate of the alkoxy and hydroxyl radicals depends upon the environment. Bimolecular decomposition can also occur as the concentration of the hydroperoxide increases [58]:

$$2\mathrm{ROOH} \rightleftharpoons \mathrm{ROOH} \cdots \mathrm{HOOR} \longrightarrow \mathrm{RO}^{\bullet} + \mathrm{RO_2}^{\bullet} + \mathrm{H_2O} \tag{20}$$

Formation of low molecular weight hydrocarbon in the decomposition of polypropylene hydroperoxides was studied by Tatarenko

and Pudov [59]. Polypropylene hydroperoxides heated in sealed ampules under argon at 130°C gave CH_4, C_6H_6, c_3H_8, $CH_2{=}CHMe$, $CH_2{=}CMe_2$, etc.

Thermal degradation of polypropylene hydroperoxide was studied by Chien and Jabloner [60]. It consisted of two consecutive reactions: The initial faster reaction, which is about 60 times faster than the slower process, and the slower reaction. The faster reaction consumes about 70-95% of the total hydroperoxides.

Chien [61] has prepared polyethylene hydroperoxide by low temperature oxidation and studied the thermal decomposition. Studies show that about 88% of the hydroperoxide group decomposes by a rapid process and the remainder decomposes at about 1/10th of that rate. The mechanism of thermal decomposition of polyethylene hydroperoxide in solution and in the solid state has been suggested.

The formation, characterization, and decomposition of polyethylene hydroperoxide were studed by Iring et al. [43]. Polyethylene hydroperoxide was prepared by the oxidation of low density polyethylene. The dependence of chemical composition and structure of hydroperoxides on the reaction conditions was studied. The rate of oxygen absorption was measured at 130°C and 760 torr pressure. In the initiated oxidation of polyethylene at 100°C, the decomposition and structure of hydroperoxide depended on the initiator, and the amount of hydroperoxide group increased in the order dicumylperoxide < benzoyl peroxide < azobisisobutyronitrile. In an inert atmosphere the decomposition rate of hydroperoxide groups decreased with the reaction time. Zolotova and Densov [62] have studied the reaction of polyethylene hydroperoxide to radicals in solution and in the solid state. The overall rate constant (k) of polyethylene hydroperoxides in both the solid state and solution was found to be the same.

The formation and decomposition of peroxides in radiation-oxidized PVC was studied by Zeppenfeld et al. [63]. PVC oxidized by radiation contains two different kinds of peroxy radicals, and 60% of the peroxy radicals decay at 20°C in oxygen atmosphere at $t_{1/2} \sim 3$ h. Forty percent of the peroxide radicals are relatively stable at room temperature, but decay at 56°C in vacuum with $t_{1/2} \sim 40$ h. The hydroperoxide decays at 50°C in vacuum with $t_{1/2} \sim 650$ h.

The chemical reaction of PVC during its oxidative thermal degradation was studied by Zilberman et al. [64]. In the oxidative thermal degradation of PVC at 170°C, the primary products of PVC-O interaction were hydroperoxides which decomposed to give carbonyl group. The content of $>CO$ groups increases while the content of hydroperoxides passed through a maximum. A reaction scheme involving chain scission with the formation of terminal carbonyl groups was proposed.

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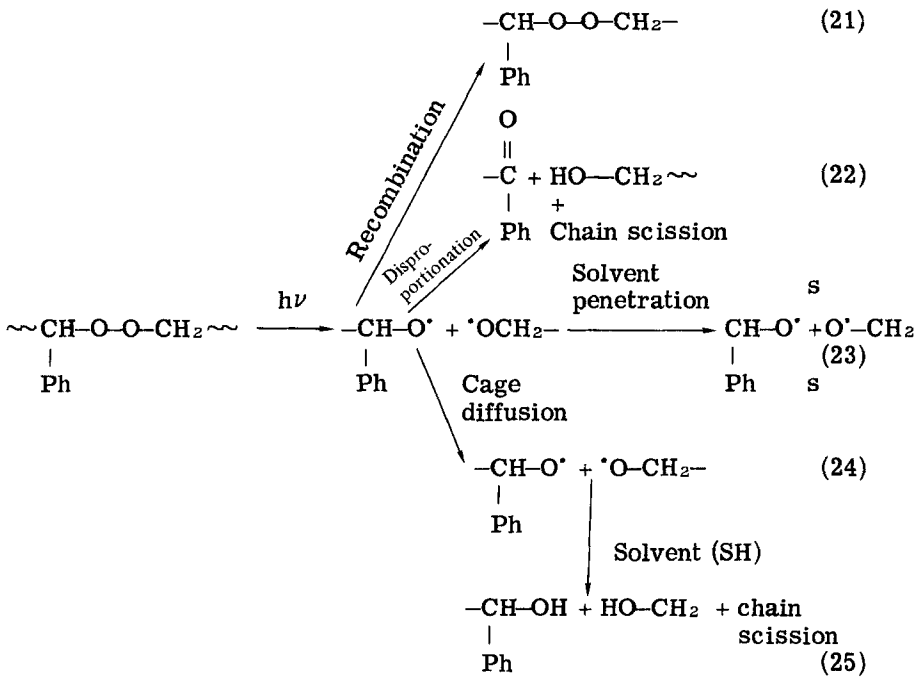
PHOTODEGRADATION OF POLYPEROXIDES AND HYDROPEROXIDES

Mayo and Miller [5] have studied the photodecomposition of polystyrene peroxide. Just like thermal decomposition, photodecomposition is a free radical chain reaction, the principal step being the homolysis of the O–O bond. The alkoxy radicals thus formed lose formaldehyde and benzaldehyde alternately. Some disproportionation products like hydroxy acetophenone and phenyl glycol are also formed along with the major products.

Weir and Milkie [65] performed photodegradation studies of polystyrene peroxide in a series of solvents. They observed a considerable change in the photolysis rate in various solvents irradiated in the same wavelength region (306 nm). They concluded that the observed difference in photodegradation was due to the different rates of abstraction of proton from solvent molecules by the alkoxy radicals formed by the initial photolysis of the O–O bond. According to them, the scission of the O–O bond produces two alkoxy radicals which may be considered to be formed in a cage. Within this cage, the alkoxy radicals can undergo different pathways as follows:



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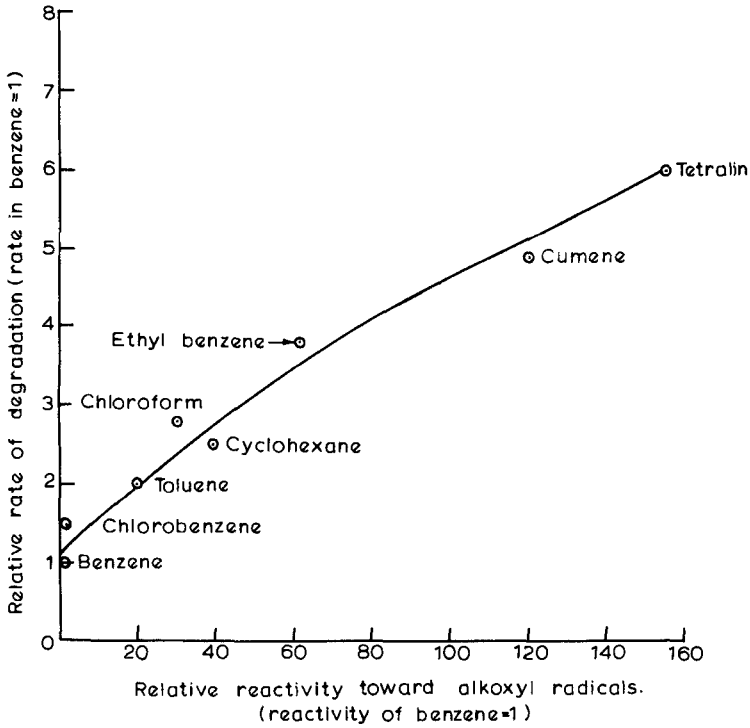

FIG. 1. Dependence of relative photodegradation rate of poly-(styrene peroxide) in various solvents on the relative reactivity of solvents toward alkoxy radicals. (Curve drawn from the data of Ref. 65.)

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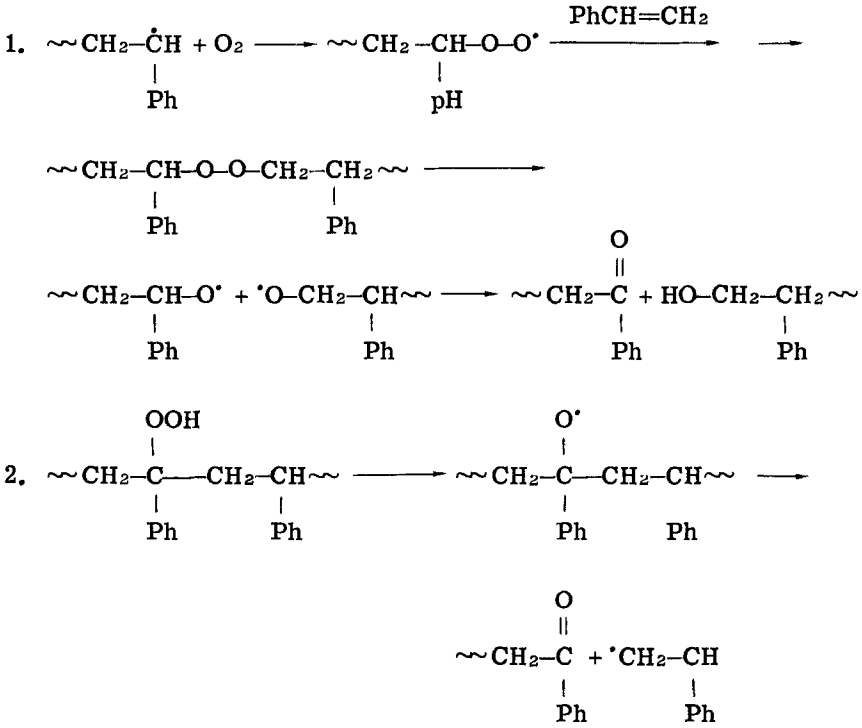
It is known that alkoxy radicals abstract hydrogen atoms even at comparatively low temperatures [66-68], the activation energy for abstraction being 20 kJ/mol [65]. If the rates of abstraction of protons from different solvent molecule by alkoxy radicals differ, this can account for the observed different rates of degradation. The abstraction step (Reaction 25) compete with the recombination step (Reaction 21). If Reaction (25) is more efficient, the rate of degradation is more and vice versa.

Figure 1 illustrates the dependence of the rate of degradation on the relative reactivity of various solvents toward alkoxy radicals. Direct evidence of solvent participation was obtained from labeled ethyl benzene in which tritium becomes chemically bound to the polymer during photolysis.

Hock and Siebert [69] showed that α-methylstyrene peroxide decomposes into acetophenone and formaldehyde by light radiations.

Mayo and Miller [5] carried out the photodecomposition studies of α-methylstyrene peroxide in benzene as well as in α-methylstyrene solution. They found that the photolysis was about 6 to 8 times slower in α-methylstyrene than in benzene. This is because α-methylstyrene is a good radical trap. It traps the alkoxy radicals formed by photolysis and thus inhibits chain reaction. Hydroquinone, oxygen, and thiophenol also retard the solution photolysis of methylstyrene peroxide. In the case of styrene peroxide photolysis, it was observed [5] that thiophenol accelerates the reaction. The $C_6H_5S^{\bullet}$ radical abstracts proton from the α-carbon atom of the styrene molecule and thus accelerates decomposition. But in α-methylstyrene peroxide, hydrogen is absent, which can account for the retarding effect of its photolysis by thiophenol.

George and Hodgeman [70] have studied the photolysis of in-chain peroxide linkages in polystyrene by phosphoresence spectroscopy. Commercial and laboratory synthesized polystyrenes contain in-chain peroxide linkages formed by the reaction of a growing polystyrenyl radical with the residual oxygen present in the monomer. These peroxide bonds may break thermally or by light radiation, resulting in phenyl alkyl ketone end groups. These end groups are responsible for the emission properties of polystyrene. Both hydroperoxides as well as in-chain peroxides can give rise to carbonyl groups by degradation:



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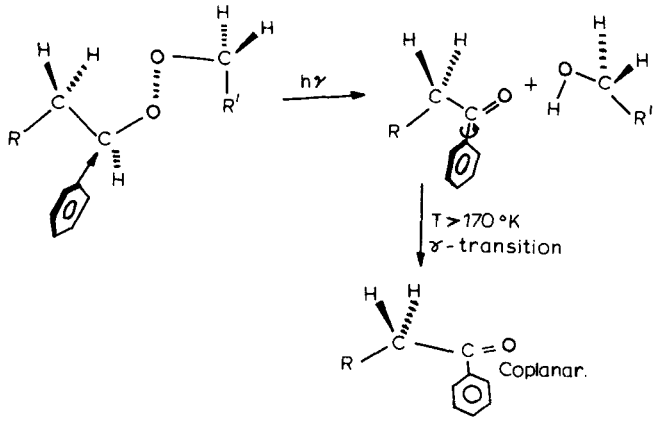
Hydroperoxides may arise in polystyrene samples by mild oxidation of the latter during the processing. However, phosphorescence studies by George and Hodgeman [70] proved that the peroxide bonds in commercial polystyrene are in-chain peroxide bonds. They prepared both hydroperoxidized polystyrene and polystyrene containing in-chain peroxides. When subjected to photolysis and phosphorescence studies, the latter gave results similar to polystyrene prior to photooxidation.

At the low temperature involved in photolysis (77 K), no emission was observed. The sample had to be heated to a certain temperature (170 K) before they could observe significant emission. At the moment of formation of the phenyl alkyl ketone end groups, the carbonyl group and phenyl ring may not be in the same plane and so there is no effective conjugation. On warming, rotation of the phenyl group occurs to bring effective conjugation, and carbonyl emission is observed:



Tsvetkov et al. [71] studied the photochemical decomposition of polymeric peroxides of adipic, pimelic, azelaic, sebacic, and 1,16-hexadecanedioic acid in various solvents. The decomposition was first-order, and the rates and mechanisms of primary decomposition reactions were solvent independent.

Formation of peroxy radicals in thin films of polyamides during irradiation in oxygen was demonstrated by Danydov et al. [72]. From kinetics of accumulation and decomposition of radicals in dark and in light, they observed that the rate of accumulation at 223 K was proportional to the square of the intensity of the light.

Carlson and Wiles [73], during their investigations on polypropylene photodegradation, observed that hydroperoxides are the chief primary product of photooxidation. They performed the photolysis of polypropylene hydroperoxide. The primary reaction is the scission of the O–O bond to form an alkoxy radical and a hydroxyl radical. The secondary reactions (of these radicals) involve abstraction of

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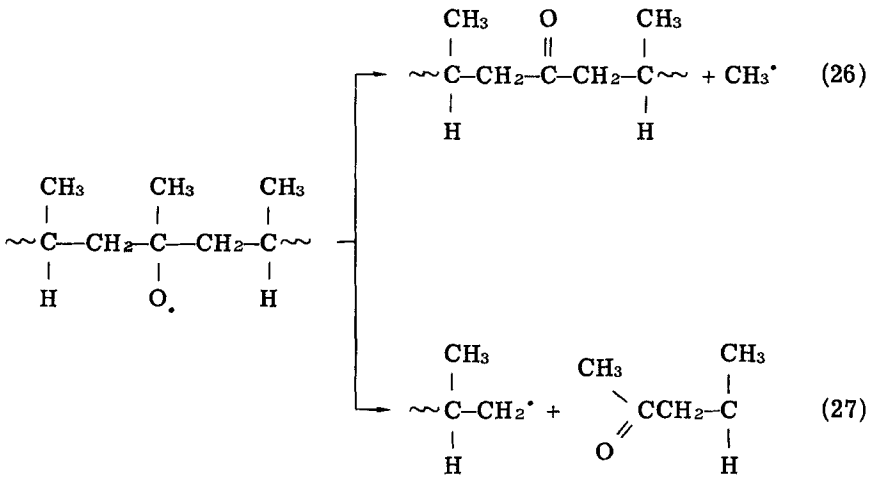
hydrogen, chain scission, disproportionation, etc., and a variety of products are formed. Water is one of the main products. Other products include CO_2, CH_4, CO, CH_3COCH_3, CH_3COOH, $HOCH_2$–$COCH_3$, CH_3OH, CH_3CHO, $CH_3COCH_2CH_3$, C_2H_6, C_2H_4, C_4H_8, and $CH_3CH(CH_3)OH$.

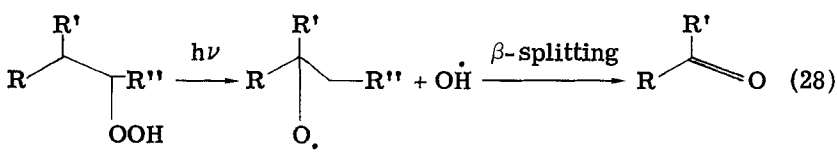
The photooxidation takes place mainly at the tertiary carbon atoms. Product analysis showed a very small amount of aldehydes which may arise from the decomposition of primary or secondary hydroperoxides. The polymeric ketones formed were characterized by IR spectroscopy by comparison with model compounds. Their formation from tertiary hydroperoxides may be explained as follows:



(26)

(27)

In contrast to alkyl peroxide radicals, the alkoxy radicals formed from photolysis of hydroperoxides undergo predominantly decomposition reactions with the splitting of polymer chains. This β-cleavage is responsible for the decomposition of polypropylene, polyethylene, polyvinyl chloride, and polystyrene [74]. In polyethylene, alkoxy radicals formed from allyl hydroperoxides lead to disproportionation and cross-linking:



(28)

Certain metallic complexes of sulfur-containing compounds are found to accelerate the decomposition of hydroperoxides [37]. One example is dialkyldithiocarbamate. These compounds have been used

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as additives for decomposing the peroxides present in preoxidized polypropylene. Thus the initiation of photooxidation by these peroxides is prevented. The mechanism of action of peroxide decomposers was not given.

Chew et al. [75] have also reported alcoholic and ketonic products in the photolysis of polyethylene hydroperoxide. The photooxidation of polyethylene is propagated by the photolysis of the hydroperoxides formed by initial photooxidation:

$$\mathrm{ROOH} \longrightarrow \mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OH} \tag{29}$$

$$\mathrm{R}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R}^{\bullet} \tag{30}$$

$$\mathrm{RO}^{\bullet} \longrightarrow \begin{matrix} \mathrm{R'} \\ \mathrm{R''} \end{matrix}\!\!>\mathrm{C{=}O} \tag{31}$$

Genskens et al. [76], during their investigations on the photooxidation of polystyrene, reported that the photolysis of hydroperoxide groups already present in polystyrene sample occurs, and the radicals thus formed initiate the photooxidation. Energy transfer takes place from the excited phenyl chromophore to the hydroperoxide groups at the irradiated wavelength (253.7 nm).

The hydroperoxide of cis-1,4-polyisoprene has been prepared and its photolysis studied [77]. When irradiated at 313 nm, the compound showed a primary quantum yield of 0.8. The subsequent radical-induced chain decomposition results in a high overall quantum yield.

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ANALYSIS OF "PEROXIDES"

Analysis of both nonpolymeric and polymeric peroxides has been presented. These are not much different because all the methods are based on the dissociation of the O–O linkage. However, the usefulness and application of a particular method depends on the stability of a particular peroxide. In order to understand the overall usefulness and shortcomings of different methods, it was thought worthwhile to present the analysis of both polymeric and nonpolymeric peroxides together.

Analysis of Organic Peroxides

Organic peroxides are oxidizers, and therefore the most common chemical method of analysis involves the reduction of the peroxide group followed by the (1) determination of excess reducing agent or

(2) the oxidized form of the reducing agent. The most commonly used reducing agent is the iodide ion [78]. Its reaction may be illustrated with a diacyl peroxide:

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + 2I \longrightarrow 2R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{-} + I_2 \qquad (32)$$

The liberated iodine may be treated with standard thiosulfate or in trace analysis determined by spectrophotometric methods [79]. Acetic acid and isopropyl alcohol are the most commonly used solvent media. Quantitative results can be obtained by using NaI in acetic acid for easily reducible peroxides such as hydroperoxides and peroxy acids. For more difficulty reducible peroxides such as di-t-butyl peroxide and some peroxy esters, a powerful reducing agent (HI) should be used at temperatures of 60-80°C. Other reducing agents which could be used are ferrous, titanous, stannous, and arsenious ions. Triphenyl phosphine has also been used as a reducing agent for peroxides [80].

Polarography is probably the most commonly used instrumental method of analysis of peroxides which are irreversibly reduced at the dropping mercury electrode. Hydroperoxides, peroxy esters, and diacyl peroxides have been determined by this method [81-83].

Organic peroxides generally absorb at 800-900 cm^{-1} in IR region. This fact has been used for analysis, particularly for kinetic studies. Gas chromatography has been used for the estimation and separation of some thermally stable hydroperoxides, peroxy esters, and dialkyl peroxides [84]. The technique [85-87] is finding increasing usage for identification and separation of peroxides in complex mixtures.

A detailed discussion of some of the chemical and instrumental methods of analysis is given in Refs. 88 and 89. Polarographic studies and those based on reduction with the iodide ion yield the following decreasing order of reactivity: Peroxy acids > hydroperoxides > diacyl peroxides > peroxy esters > dialkyl peroxides. Within each group there is a large variation in reactivity. Because of this variation in reactivity between different classes, and within each class, there is neither a single general method of analysis for all peroxides nor for each group.

A review on the qualitative and quantitative analysis of organic peroxides, including iodometric, arsenometric, stannometric, titanometric, as well as liquid, gas-liquid, paper, and thin-layer chromatographic methods, has been presented by Antouovskii and Buzlanova [90].

Analysis of Polymeric Peroxides

The techniques employed for the analysis of simple organic peroxides cannot be applied to polymeric peroxides because of incorporation

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of the peroxy group in a long polymeric chain. Titrimetric procedures, including the iodometric method, have limited usefulness. Although a completely satisfactory procedure could not be found, Miller and Mayo [5, 6] have estimated styrene peroxide iodometrically using constant boiling hydroiodic acid and mercaptans.

Beachell and Smiley [41] have estimated the polymeric hydroperoxide formed during PS oxidation in $CHCl_3$ by using benzoyl leuco methylene blue as the coloring agent [91]. A colorimetric method for the determination of polypropylene hydroperoxide was also developed by Bocek [92] based on methylene blue leucobase. The method is applicable for the determination of 10^{-8} to 30×10^{-7} mol hydroperoxide.

NMR has proved a most useful tool for the analysis of the detailed structure of polymeric peroxides. Because of strong deshielding by the oxygen, α-hydrogen ($-CHO_2-$) is shifted downfield from the corresponding hydrogen-substituted structure ($-CH$) by about 2 τ units. β-Hydrogen show somewhat smaller shifts [3].

Novak [93] has determined the hydroperoxides in styrene polarographically. A linear relationship between the limiting current at the peroxide and peroxide concentrations was observed.

A complexometric method for the determination of peroxide in styrene has been reported by Turuta and Mariapal [94]. Ferrous ammonium sulfate in H_2SO_4 is added to styrene containing peroxide, and the resulting ferric ion is treated with EDTA in the presence of sulfosalicylic acid, maintaining the pH at 2.

Mironova and Smitnov [95] have determined the hydroperoxide content in polyamide with a $\leq \pm 14\%$ error by dissociation with $HCO_2\phi H$, treatment with acetic acid and aqueous HI, and measurement at an absorbance of 325 nm.

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CONCLUSION

The information available in the literature on various aspects of polymeric peroxides has been brought together so that the matter can be examined critically. It can be seen that like all peroxides, polymeric peroxides also decompose fairly readily. The polymeric peroxide of butadiene is considered potentially more sensitive than even trinitrotoluene. Most of the peroxides are relatively soluble in the parent monomer, but the polymeric peroxide of butadiene is not. Once it is formed, even in low concentrations, it becomes concentrated by separating out. Thus there is a need to develop some safer methods of preparation and handling techniques. Not much work has been emerged on the photodegradation studies of polymeric peroxides. The exact mechanism by which in-chain peroxides decompose in the solid state is yet to be investigated.

Satisfactory results have not been obtained by any method of analysis described in the literature for all types of polymeric peroxides.

Chemical methods have limited usefulness. Instrumental methods (NMR, etc.) have to be fully explored to get quantitative results. Thus a quicker and more reliable method of analysis has to be developed.

It is very difficult to analyze hydroperoxides and in-chain peroxides separately in a mixture. Therefore, a clear-cut and reliable method for the analysis of polyperoxides and hydroperoxides in a mixture is necessary.

REFERENCES

[1] G. H. Dale, "Peroxides, Polymeric," in Encyclopedia of Polymer Science and Technology, Vol. 9, 1968, p. 807.
[2] O. L. Mageli and C. S. Sheppard, "Peroxides and Peroxy Compounds, Organic," in Encyclopedia of Chemical Technology, Vol. 14, 1967, p. 766.
[3] O. L. Mageli and J. R. Kolezynski, "Peroxy Compounds," in Encyclopedia of Polymer Science and Technology, Vol. 9, 1968, p. 814.
[4] A. G. Davies, Organic Peroxides, Butterworths, London, 1961.
[5] A. A. Miller and F. R. Mayo, J. Am. Chem. Soc., 78, 1017 (1956).
[6] F. R. Mayo and A. A. Miller, Ibid., 78, 1023 (1956).
[7] E. D. Van Sickle, F. R. Mayo, R. M. Arluck and G. Syz. Martin, Ibid., 89, 967 (1967).
[8] F. R. Mayo, J. K. Castelman, T. Mill, R. M. Silverstein, and O. Rodin, J. Org. Chem., 39(7), 889 (1974).
[9] F. R. Mayo, A. A. Miller, and G. A. Russel, J. Am. Chem. Soc., 80 2500 (1956).
[10] F. R. Mayo, Ibid., 80, 2465 (1958).
[11] F. R. Mayo, Ibid., 80, 2497 (1958).
[12] F. R. Mayo and A. A. Miller, Ibid., 80, 2480 (1958).
[13] E. D. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, Ibid., 89, 977 (1967).
[14] V. V. Korshak, V. A. Sergeev, and V. G. Pokrikyan, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 61, 1100 (1963); Chem. Abstr., 59, 7650g (1973).
[15] L. Dulong, J. Szira, and W. Kern, 6th Wiesbaden, p. 209 (1962); Chem. Abstr., 58, 4738g (1963).
[16] Pingchang and Yu Lin Tien, Hua Hsuch Hsuch Pao, 24, 135 (1958); Chem. Abstr., 53, 7000g (1959).
[17] F. R. Mayo and A. A. Miller, J. Am. Chem. Soc., 80, 2493 (1958).
[18] R. Kerber, Makromol. Chem., 40, 25 (1960).
[19] D. G. Hendry, F. R. Mayo and D. Schuetzle, Ind. Eng. Chem., Product Research and Development, 7(2), 136 (1968).
[20] W. H. Hutchinson, U.S. Patent 3,023,249 (1962); Chem. Abstr., 57, 8439a (1962).

Downloaded At: 07:44 25 January 2011

[21] L. Chodak and S. Suta, Sbornik Praci Khim. Fakulty SVST, p. 141 (1967); Chem. Abstr., 69, 60117C (1968).
[22] T. O. Craig and E. Tyrrall, J. Polym. Sci., Part B, 5(10), 955 (1967).
[23] G. S. Bylina, L. K. Burykina, and Y. A. Oldekop, Vysokomol. Soedin., Ser. B, 12(9), 670 (1970); Chem. Abstr., 74, 3896K (1971).
[24] G. A. Razuvaev and K. S. Minisker, Zh. Obshch. Khim., 28, 983 (1958).
[25] W. O. Lundsberg (ed.), Autoxidation and Antioxidants, Wiley-Interscience, New York, Vol. 1, 1961; Vol. 2, 1962.
[26] E. J. Vandenberg, U.S. Patent 2,911,391 (1959); Chem. Abstr., 54, 4042C (1960).
[27] L. A. Wall, M. R. Harvey, and M. Tryon, J. Phys. Chem., 60, 1306 (1956).
[28] M. Tryon and L. A. Wall, Ibid., 62, 697 (1958).
[29] A. Chapiro, Natl. Bur. Stand. (U.S.), Spec. Pub. 357, 79 (1972); Chem. Abstr., 78, 148406t (1973).
[30] H. M. G. Jellinek, Trans. Faraday Soc., p. 266 (1944).
[31] H. H. G. Jellinek, Ibid., p. 345 (1948).
[32] H. H. G. Jellinek, J. Polym. Sci., 3, 850 (1948).
[33] H. H. G. Jellinek, Ibid., 4, 1 (1949).
[34] G. Geuskens, D. Balyens-Volant, G. Delauneis, Cl. Lu. Vinh, W. Piret, and C. David, Eur. Polym. J., 14(4), 291 (1978).
[35] Y. Kato, D. J. Carlsson, and D. M. Wiles, J. Appl. Polym. Sci., 13(7), 1447-1458 (1969).
[36] N. Gassie and N. A. Weir, Ibid., 9, 987 (1965).
[37] H. Lind, Kunststoffe, 69, 397-402 (1979).
[38] M. Tryon and L. A. Wall, J. Phys. Chem., 62, 697 (1958).
[39] H. C. Beachell and S. P. Nemphol, J. Polym. Sci., 25, 173 (1957).
[40] B. G. Achhammer, Reinley, L. A. Wall, and F. W. Renhart, J. Polym. Sci., 8, 555 (1952).
[41] H. C. Beachell and L. H. Smiley, J. Polym. Sci., Part A-1, 5, 1635 (1967).
[42] Yakimenlako, Izv. Akad. Nauk, SSSR, 2, 354 (1974).
[43] Mrs. R. Iring, T. Kelene and F. Tudos, Magy. Kem. Foly., 82(5), 244 (1976).
[44] Mrs. R. Iring, H. Z. Laszlo, T. Kelene, F. Tudos, L. Fuses, G. Samay, and G. Bodor, Ibid., 82(5), 252(1976); Chem. Abstr., 85, 33646y (1976).
[45] Mrs. R. Iring, T. Kelene and F. Tudos, Ibid., 80(3), 97 (1974); Chem. Abstr., 81, 106051e (1974).
[46] M. Iring, T. Kelen, and F. Tudos, Makromol. Chem., 175(2), 467 (1974).
[47] Mrs. R. Iring, T. Kelen, and F. Tudos, Magy. Kem. Foly., 81(7), 298 (1975); Chem. Abstr., 83, 132235d (1975).
[48] M. Iring, T. Kelene, and F. Tudos, Eur. Polym. J., 11(9), 631 (1975).

Downloaded At: 07:44 25 January 2011

[49] N. V. Zolotova and E. T. Denisov, Vysokomol. Soedin., Ser. B, 12(12), 866 (1970); Chem. Abstr., 74, 54333g (1971).
[50] A. A. Miller and F. R. Mayo, U.S. Patent 2,767,208 (1956); Chem. Abstr., 51, 4433b (1957).
[51] N. S. Tsvetkov and R. F. Markovskaya, Kinet. Katal., 10(1), 57 (1969); Chem. Abstr., 70, 106964C.
[52] K. Kishore, V. R. Pai Verneker, and V. Gayathri, J. Anal. Appl. Pyrol., In Press.
[53] K. Kishore, J. Therm. Anal., In Press.
[54] N. S. Tsvetkov, R. F. Markovskaya, and V. Ya. Zhukovskii, Kinet. Katal., 17(4), 883 (1976); Chem. Abstr., 85, 160795W (1976).
[55] N. S. Tsvetkov, R. F. Markovskaya, and V. Ya. Zhukovskii, Visn. L'viv. Derzh. Univ., Ser. Khim., 18, (1976); Chem. Abstr., 85, 160792t (1976).
[56] F. Dutka and D. Gal, Atompraxis, 5, 445 (1959); Chem. Abstr., 54, 9458C (1960).
[57] A. A. Miller and F. R. Mayo, U.S. Patent 2,767,208 (1958); Chem. Abstr., 51, 4433b (1957).
[58] J. R. Shelton and D. N. Vincent, J. Am. Chem. Soc., 85, 2433 (1963).
[59] Tatarenko and Pudov, Vysokomol. Soedin., Ser. B, 10(4), 287 (1968); Chem. Abstr., 68, 50264P (1968).
[60] J. C. W. Chin and H. Jabloner, J. Polym. Sci., Part A-1, 6(2), 393 (1968).
[61] J. C. W. Chien, Ibid., 6(2), 375 (1968).
[62] N. V. Zolotova and E. T. Densov, Vysokomol. Soedin., Ser. B, 12(12), 866 (1970); Chem. Abstr., 74, 54333g (1971).
[63] G. Zeppenfeld and A. Bartl, J. Polym. Sci., Part C, 16(8), 4369 (1969).
[64] E. N. Zilberman, E. M. Perepletchikova, and E. N. Getamanenko, Izv. Vyssh. Uchebn. Zabed., Khim. Khim. Technol., 19(8), 1255 (1976); Chem. Abstr., 85, 160793u (1975).
[65] N. A. Weir and T. H. Milkie, Makromol. Chem., 179, 1989-1998 (1978).
[66] P. Gray, R. Shaw, and J. C. J. Thynne, Prog. React. Kinet., 4, 63 (1968).
[67] R. L. Huong, J. W. Lee, and S. H. Ong, J. Chem. Soc., C, p. 40 (1969).
[68] L. Dulong and K. H. David, Makromol. Chem., 177, 1717 (1976).
[69] H. Hock and M. Siebert, Chem. Ber., 87, 546 (1954).
[70] G. A. George and D. K. C. Hodgeman, Eur. Polym. J., 13, 63-71 (1977).
[71] R. F. Markovskaya, N. S. Tsvetkov, E. S. Yakhimovich, V. Ya. Zhukovski, and A. R. Babich, Tezisy Dokl. Resp. Konfg. Vyskomol. Soedin., 3, 24 (1973); Chem. Abstr., 84, 97750q (1976).
[72] E. Ya. Danydov, A. L. Margolin, G. B. Pariiskii, L. M. Postinikov, and D. Ya. Toplysin, Dokl. Akad. Nauk SSSR, 243(6), 1475-1478 (1978); Chem. Abstr., 90, 138378u (1979).

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[73] D. J. Carlsson and D. M. Wiles, Macromolecules, 2, 597-606 (1969).
[74] D. J. Carlsson and D. M. Wiles, Ibid., 2, 587 (1969).
[75] Ch. Chew, L. M. Gan, and G. Scott, Eur. Polym. J., 13(5), 367 (1977).
[76] G. Genskens, D. Balegens-Volant, G. Delaumis, Q. Lu-vinh, W. Piret, and C. Dadid, Ibid., 14(4), 299-303 (1978).
[77] N. G. Howard and J. E. Guillet, Macromolecules, 11(5), 929 (1978).
[78] R. D. Mair and A. J. Graupner, Anal. Chem., 36, 194 (1964).
[79] D. K. Banerjee and L. L. Budke, Ibid., 36, 2367 (1964).
[80] L. Dulog and K. H. Burg, Z. Anal. Chem., 203, 184 (1964).
[81] L. Dulog, Ibid., 202, 258 (1964).
[82] T. T. Yurzhenko et al., Dokl. L'vov. Politekh. Inst., Khim. Khim. Technol., 5, 41 (1963).
[83] V. N. Pavlov et al., Zavod. Lab., 30, 539 (1964).
[84] S. W. Bukata, L. L. Zabrocki, and M. F. McLaughlin, Anal. Chem., 35, 855 (1963).
[85] M. M. Buzlanova et al., Zh. Anal. Khim., 21, 506 (1966).
[86] S. Hayano et al., Jpn. Anal., 15, 365 (1966).
[87] G. Dobson and G. Hughes, J. Chromatogr., 16, 416 (1964).
[88] D. J. Martin, J. Mitchell, Jr., J. M. Kolthoff, E. S. Proskaner, and A. Weissberger (eds.), Organic Analysis, Vol. 4 Interscience, New York, 1960.
[89] S. Siggia, Quantitative organic analysis via functional group, 3rd ed., Wiley, New York, 1963, p. 255.
[90] V. L. Antonovskii and M. W. Buzlanova, Obz. Otd. Proizvod. Khim. Promsti., 45, 40 (1973).
[91] M. I. Eiss and P. Griesecke, Anal. Chem., 31, 1553 (1968).
[92] P. Bocek, Chem. Prum., 17(4), 216 (1967); Chem. Abstr., 68, 3193C (1968).
[93] V. Novak and J. Malinsky, Plaste Kautsch., 15(10), 722A (1968); Chem. Abstr., 70, 4632a (1969).
[94] A. Turuta and Mariapal, Rev. Chim., 17(2), 765 (1966); Chem. Abstr., 66, 95402g (1967).
[95] Z. I. Mironova and C. N. Smirnov, Volkona Sin. Polim., p. 287 (1970); Chem. Abstr., 74, 112600e (1971).

Accepted by editor October 31, 1980
Received for publication January 8, 1980

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