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Role of Oxygen in Polymerization Reactions

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I. Introduction

In the fascinating world of polymers, their interaction with aerial oxygen during commercial polymerization and environmental degradation is conspicuously unavoidable. A perusal of the pertinent literature reveals that the role of oxygen in polymer synthesis is comparatively less understood than its effect on polymer degradation which has been well documented.[1-5] In polymer synthesis, since oxygen can both initiate and inhibit polymerization processes, its involvement is intriguing. Inspite of the obvious importance of this topic in polymer chemistry, hitherto no attempt seems to have been made to review the subject by simultaneously considering the contrasting roles of oxygen mentioned above. We have therefore attempted in this review to judiciously sift through the literature scattered over a span of several decades and to articulate in a comprehendable fashion the elusive role of oxygen in polymerization reactions.

Oxygen plays a very significant part in various polymerization reactions, particularly when organometallic initiators or catalysts are involved. The exact role of oxygen, however, is not well understood and reports in the literature are scattered. The subject appears to be interdisciplinary in nature, involving organometallic chemisitry, catalysis, organic reaction mechanisms, and polymer chemistry. Furthermore, no monograph on this subject is available. Though a few articles[6-15] are available in the early literature, they deal only with some specific reactions like emulsion polymerization of some acrylic monomers.[8] Relatively very little attention has been paid previously to the inhibitory action of oxygen in polymerization processes. The earlier studies, in this regard, focused attention mainly on radical polymerization reactions. The results are paradoxical since some reports maintained that oxygen aids to initiate the polymerization reactions rather than to inhibit it. Bovey and Kolthoff[16] have summarized these conflicting views and have shown how enigmatic the role of oxygen is in radical polymerization. A detailed understanding of the parts played by oxygen in polymerization reactions is therefore necessary.

Reports on the effect of oxygen on various polymer properties are available (see section V and references therein). These range from fundamentally important properties like molecular weight distribution and tacticity, to commercially important bulk properties such as mechanical and thermal properties, etc. However, most of these studies are patented. Apparently, oxygen brings about irreversible changes in polymer properties, most often producing undesirable effects. For example, the conductivity of polyacetylene is gradually lost on exposure to aerial oxygen. Nevertheless, in some specific instances, the role of oxygen can be advantageous. This is evident in the case of lithium-terminated poly-

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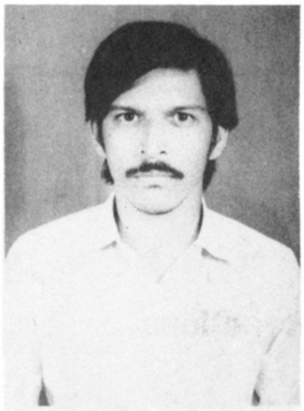

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styrene. The highly reactive end group of this polymer yields a hydroperoxide-terminated polymer upon reaction with oxygen. Such telechelic polymers are potential precursors for the synthesis of novel block copolymers.

In order to succinctly present all the important developments in this vast but interesting area of active research, we have organized this review in the following framework: (i) kinetics and mechanism of polymerization reactions, (ii) activity of various catalysts and cocatalysts of polymerization processes, and (iii) properties of polymers. We earnestly hope that this review will be able to clear the mist over the perplexing role of oxygen, that it may help those working in the field to assess the progress achieved in this area, and that it may be useful orientation to those who want to become involved in this area.

II. Role of Oxygen in the Initiation of Polymerization

A. Kinetics and Mechanistic Studies

Although many papers and patents mention the use of oxygen either as a cocatalyst or promoter of polymerization, only in a few cases is the mechanism of initiation of oxygen reported. It is established that oxygen can initiate the high-pressure polymerization of ethylene, and it is a part of the redox initiators for (i) oxidative coupling of phenols and (ii) free-radical polymerization of vinyl monomers. In all the reactions mentioned here interaction of oxygen with the other species, particularly in the initiation stage, produces labile intermediates which complicate the pellucid understanding of these reactions. Hence more emphasis has been given in recent times to understanding the chemistry of the initiation step of these reactions, which are discussed below.

1. Ethylene Polymerization

Low density polyethylene, one of the most commonly used polymer, is prepared by compressing ethylene gas up to a pressure of 1000–3000 atm and using aerial oxygen as initiator. Although oxygen was used as a cheap initiator[17] as early as 1937, the exact role of oxygen in this polymerization reaction remained a debatable topic until recently.[18–20] To cite an example, Ehrlich et al.[19] while studying the polymerization of ethylene up to 2000 atm and at temperatures below 180 °C found that polymerization does not take place below a critical pressure, which depends upon the initial oxygen concentration. On the other hand, Gierth[20] found that during the polymerization of ethylene up to 150 atm and below 170 °C, no "critical pressure" phenomenon exists! Another unclear aspect is the size and reactions taking place during the induction period and its duration. Although a significant induction period was noticed in the earlier work of Ehrlich[19] and others,[21,22] the reproducibility of the data is poor.[23] More recently, an induction period has also been observed by Tatsukami et al.[23] in what they claim as a more reliable study of this reaction at 175 °C and 1355 atm. Although a copolymerization of oxygen and ethylene was suggested[19] to be a possible product during the induction period, a recent study[23] showed that oxygen does not react with ethylene during this time period. Tatsukami et al.[23] also found that in order to obtain the same rate of polymerization, considerably larger quantities of oxygen has to be used as an initiator than in the di-*tert*-butyl peroxide.

The study of Tatsukami et al.[23] clearly demonstrates the unique feature of high-pressure ethylene polymerization—oxygen acts as both an initiator as well as an inhibitor in this reaction. The kinetic scheme for polymerization of ethylene in the temperature range of 190–230 °C and pressure of 1355 atm is discussed:

$$\text{initiation} \qquad O_2 + C_2H_4 \xrightarrow{k_d} 2r_0^\bullet \tag{1}$$

$$\text{propagation} \qquad r_0^\bullet + C_2H_4 \xrightarrow{k_p} r_1^\bullet \tag{2}$$

$$\text{retardation} \qquad r_n^\bullet + O_2 \xrightarrow{k_r} \text{deactivated products or hydroperoxides} \tag{3}$$

$$\text{termination} \qquad r_n^\bullet + r_m^\bullet \xrightarrow{k_t} P_{n+m} \tag{4}$$

All the k's in the above and subsequent equations represent the rate constant values. As evident from the above scheme, oxygen produces initiating radicals (eq 1) as well as terminates the propagating radicals (eq 3). Hence,

$$\frac{d[O_2]}{dt} = -k_d[O_2][C_2H_4] - k_t[O_2]\sum_{n=0}^{\infty}[r_n^\bullet] \tag{5}$$

and

$$\frac{d[C_2H_4]}{dt} = -k_p[C_2H_4]\sum_{n=0}^{\infty}[r_n^\bullet] \tag{6}$$

$$\frac{d}{dt}[\sum_{n=0}^{\infty}[r_n^\bullet]] = k_d[O_2][C_2H_4] = k_r[O_2]\sum_{n=0}^{\infty}[r_n^\bullet] = k_t[\sum_{n=0}^{\infty}[r_n^\bullet]^2]^2 \tag{7}$$

Assuming a steady state with respect to the radical concentration, the right-hand side of eq 7 becomes zero. Solving the quadratic equation with respect to $[r_n^\bullet]$ and neglecting the term $[O_2]^2$ because of its low concentration (10^{-4} mol L^{-1}), one obtains the following equation for the total radical concentration.

$$\sum_{n=0}^{\infty}[r_n^\bullet] = \frac{-k_r}{2k_t}[O_2] + \frac{k_d^{1/2}}{k_t^{1/2}}[C_2H_4]^{1/2}[O_2]^{1/2} \tag{8}$$

Substitution of eq 8 into eqs 5 and 6 yields

$$\frac{d[O_2]}{dt} = -k_d[O_2][C_2H_4] = \frac{k_r k_d^{1/2}}{k_t^{1/2}}[C_2H_4]^{1/2}[O_2]^{3/2} \tag{9}$$

$$R_p = \frac{-d[C_2H_4]}{dt} = -\frac{k_p k_r}{2k_t}[C_2H_4][O_2] + \frac{k_p k_d^{1/2}}{k_t^{1/2}}[C_2H_4][O_2]^{1/2} \tag{10}$$

Numerical calculations made with use of eqs 9 and 10, and by adopting appropriate values of the rate constants show that the results agree well with the experimentally observed conversion of ethylene as a function of time. The above model assumes that the deactivated products like the hydroperoxide does not undergo thermal decomposition yielding radicals which may complicate the process.

The above model is very simple and clearly demonstrates the exactly opposite roles of oxygen in the same polymerization process. However, the model is useful only to explain the reaction carried out above 175 °C when no induction period is observed. The reaction carried out at lower temperatures is preceded by a significant induction period during which oxygen appears to be in some sort of equilibrium with ethylene, a situation difficult to explain on basis of the above model.

It is worth mentioning at this stage, the report on the effect of oxygen on peroxide-initiated ethylene polymerization; it was observed[24] that oxygen can neither initiate nor inhibit the polymerization up to 160–170 °C. On the other hand, at temperatures higher than this, at which oxygen could alone initiate the high-pressure ethylene polymerization, an interesting behavior was noticed. The conversion obtained from the simultaneous addition of oxygen and peroxide was lower than that obtained by summing up the conversion from separate polymerization experiments. This was attributed to the inhibitory action of oxygen in peroxide-initiated polymerization. In light of the work of Tatsukami et al.[23] this result can now be attributed to the poor efficiency of oxygen as an initiator compared to the peroxide. Obviously, oxygen prefers to undergo a more facile retardation reaction (like the one depicted in eq 3) thereby reducing the yield of the simultaneous initiation experiment.

TABLE I. Polymerization of Polar Monomers by Organometallic Compounds–Oxygen (OMC–O_2) Initiator Systems

monomer[a]	initiator	10^2 × molar ratio O_2–OMC	time, h	temp, °C	polymer yield, %	ref
VAc	$B(C_2H_5)_3$	14.3	20	30	40	25
MMA	$B(C_2H_5)_3$	6.5	0.5	30.1	14	25
VC	$B(C_4H_9)_3$	9.5	3	20	20	25
AN[b]	$B(C_4H_9)_3$	–	0.8	0	4.2	25
VA	$Al(C_2H_5)_3$	50	24	25	12	25
VC[c]	$Al(C_2H_5)_3$	–	4	−17	3	25
MMA	$Cd(C_2H_5)_3$	6.9	21	20	14	25
Sty	$B(C_2H_5)_3$	–	2	20	0	27
NBE	$B(C_2H_5)_3$	–	2	20	0	27

[a] VAc = vinyl acetate; VC = vinyl chloride; AN = acrylonitrile; Sty = styrene; NBE = *n*-butyl vinyl ether. [b] In a sealed tube in air. [c] Experiment was carried out in a stream of dry and purified air flowing at a constant rate of 50 mL min^{-1}. The concentration of $Al(C_2H_5)_3$ in petrol is expressed as a weight percentage; molar ratio VC–$Al(C_2H_5)_3$ = 7.28/1.

2. Trialkylboranes–Oxygen as Initiators of Free-Radical Polymerization

Many organometallic compounds (particularly of group III elements) in combination with oxygen or peroxy compounds act as efficient initiators for radical polymerization reactions at low temperatures.[25] The data in Table I shows that (1) the most active of these compounds are the organoboranes and (2) the combination of trialkylboranes–oxygen (R_3B–O_2) can initiate the polymerization of polar monomers more efficiently than less polar monomers like styrene.[26] These initiator systems are, therefore, considered to be monomer selective. Because of their better efficiency R_3B–O_2 initiators have been studied more extensively and hence are more emphasized in the following discussion.

Trialkylboranes (R_3B) alone do not polymerize the vinyl monomers but significant polymerization takes place in the presence of oxygen. It may then be expected that the oxidation of trialkylboranes also proceeds through the formation of free-radical intermediates capable of initiating the polymerization of added monomer. The commonly accepted[27-29] mechanism of oxidation of trialkylboranes does corroborate this view:

$$R_3B + O_2 \rightarrow R_2BOO^\bullet + R^\bullet \tag{11}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{12}$$

$$R_3B + ROO^\bullet \rightarrow R_2BOOR + R^\bullet \tag{13}$$

In addition to these, following radical-generating reaction between a borane and its peroxide derivative, is also known:[28,29]

$$R_2BOOR + R_3B \rightarrow R_2BOR + R_2BO^\bullet + R^\bullet \quad (14)$$

A recent gas chromatographic study[29] of the degradation reaction of triisobutylborane by oxygen, *tert*-butyl hydroperoxide, and *tert*-butyl peroxide indicates the formation of isobutane, isobutyl alcohol, and formaldehyde. Isobutyl and isobutoxy radicals are therefore considered to have formed by a reaction similar to that depicted in eq 12.

Although the polymerization reactions initiated by R_3M–oxygen pairs, where M represents elements other than boron in Table I follow radical mechanism, the radical-generating reaction may vary for each case. For example, the following redox reaction is found[30] to occur in the case of ethylaluminum alkyl-initiated polymerization:

$$>Al{-}R + >Al{-}O{-}O{-}R \rightarrow >Al{-}O{-}Al< + R^\bullet + RO^\bullet \quad (15)$$

which is different than the reaction (14). Detailed mechanistic studies, particularly on the initiation step, are not available for the polymerization reactions initiated by organometallic compounds of heavier members of group III elements. This is because the intermediates formed during the oxidation of such organometallic compounds are too reactive to isolate; the first report on a peroxide derivative of indium has appeared only recently.[31]

The above mechanism indicates that radicals responsible for the initiation of polymerization are generated not only by the conventional autooxidation-like process, but also by the reaction depicted in eq 14. It may be expected from eq 14 that partially oxidized trialkylboranes are less efficient initiators for radical polymerization since they can generate a lesser number of radicals than the parent organoborane compound. Experimentally, this has been found[25] to be true. It has also been observed[25,27] that organoborane compounds containing electron-donor groups are less efficient than the parent trialkylboranes. In other words, the following order holds true for the ease of oxidation, and the efficiency of the initiation of polymerization:

$$R_3B > (RO)BR_2 > (RO)_2BR \text{ and}$$

$$R_3B > R_2BCl > RBCl_2$$

This behavior is explained[25] from the fact that the electron-donor groups which can donate electrons intermolecularly or intramolecularly to the unfilled shell of the boron atom, render the organoboron compounds less susceptible to an attack by oxygen, and also, less efficient initiators. Variation in the rate of oxidation of organoaluminum compounds follows the same order as mentioned above for the organoboron compounds; the ratios of the rates of oxidation of Et_3Al, $Et_2Al(OEt)$, and $EtAl(OEt)_2$ are 100:25:1.[32]

Assuming for the sake of simplicity that the polymerization reactions initiated by R_3B–oxygen type initiators are generated by reaction (11) alone, the following rate expression may be derived:

$$R_p = k[M][O_2]^{1/2} \text{ (at constant } [R_3B]) \quad (16)$$

where [M] is initial monomer concentration. Welch,[33] in fact, found this expression to be valid for an Et_3B–oxygen initiated MMA polymerization. Further, on the basis of the results of Talamini and Viddoto,[34] a similar expression was also derived by Reich and Schindler[15] for the polymerization of vinyl chloride. However, Welch[33] did observe that low conversions are obtained under two extreme conditions—either $[R_3B] \gg [O_2]$ or $[R_3B] \ll [O_2]$. He explained this observation by arguing that both R_3B and its monoperoxide derivative should necessarily be present to generate enough primary radicals for initiating the polymerization. Under the first extreme condition given above, inadequate amount of the monoperoxide is formed, while in the other extreme case all the trialkylborane is consumed to form the peroxide. This work prompted Hansen[35] to carry out a detailed study of Et_3B–O_2-initiated polymerization of MMA. He found that the simple rate expression 16 is valid only at the very beginning of the polymerization. According to Hansen,[35] in systems of this type a number of competing reactions take place and lead to the formation of free radicals capable of initiating the polymerization, which complicates the analysis of the kinetics of the overall process. He also found[36] that apart from the reaction 14, another redox reaction between the monoperoxide and partially oxidized R_3B takes place to generate the radicals. The rate of such a reaction is, however, very slow.

$$>B{-}O{-}O{-}R + >B{-}O{-}R \xrightarrow{\text{slow}} R^\bullet + BO^\bullet \quad (17)$$

Similar reactions involving di- or trialkoxy derivatives of the trialkylborane are also possible. Since the initial ratio of $[R_3B]/[O_2]$ decides the quantity of all the peroxidic products, contribution of the redox reactions 14 and those like 17 to the initiation process would also depend on this ratio. This would lead to significant changes in the observed kinetics of the polymerization when the initial ratio $[R_3B]/[O_2]$ is varied. R_3B–O_2 is a rare type of binary initiators, as variation in the concentration of their components over a small range significantly shifts the preeminence of the initiation reaction 14 to that like 17, and thereby changes the overall kinetics of the process. Hansen[35] indeed found that for an Et_3B–oxygen-intiated MMA polymerization three different shapes of conversion versus time curves are obtained depending upon the initial ratio $[Et_3B]/[O_2]$ (<1, 1–2, >3). It is evident from the above discussion that initiation step of the R_3B–O_2-initiated polymerization reactions is a concerted process.

The variation in the reactivity of organometallic compounds oxidized to different stages was also noticed in the case of Zn and Al compounds. It was reported by Nakayama et al.[37] that systems based on alkoxy derivatives of Zn in combination with peroxides are more active than those based on zinc alkyls. Similarly, in the case of aluminum derivatives, monoalkoxyaluminum and oxygen or hydroperoxide-based systems are more active polymerization catalysts.[25]

Another controversial aspect of trialkylborane–oxygen-initiated reactions pertains to the role of monomer in the initiation step. Furukawa et al.[26] found that the R_3B–oxygen system can initiate the polymerization of electron-donor-type monomers like MMA, vinyl acetate, or acrylonitrile but not of monomers like styrene. This was explained by assuming that reaction is initiated by anionic mechanism. Welch[33] suggested that monomer selectivity in this type of polymerization may arise from differences in the oxygen absorption capacity of the monomers. Complexation of the monomer with R_3B was also evoked to explain this monomer-selective polymerization. For example, Bawn et al.[38] had proposed that a complex is formed between trialkylborane and MMA, although no evidence was provided for the same. On the other hand, in the presence of Et_3B, Fuji et al.[39] observed splitting of the carbonyl absorption band of vinyl acetate into 1754 and 1774 cm^{-1} bands, ascribing it to the formation of a complex between Et_3B and the monomer. Davies[40] suggested that the boroperoxide and the monomer may be forming a complex which undergoes O–O bond homolysis and induces the polymerization. He also mentioned that the situation differed from that of Bawn et al.[38] for polymerization of MMA in that no molecule of R_3B is involved in the complexation with the monomer.

In the background of the controversial reports mentioned above, a more revealing study has been recently conducted by Dodonov et al.[41] to analyze the role of monomer in Me_3SiOOR''–R_3B-initiated polymerization of vinyl monomers. Similar to R_3B–O_2 system, here too, the selectivity in polymerizing certain monomers was observed; styrene, MMA, and vinyl chloride could be polymerized, but not acrylonitrile. Based on a detailed spin-trapping study of the polymerization reaction, Dodonov et al.[41] proposed the following initiation step, which is actually a concerted process involving monomer participation.

$$R_3B + Me_3SiOOR'' \rightleftharpoons \underset{A}{[R_3B\cdot Me_3SiOOR'']}$$

$$A + \text{monomer (M)} \rightarrow \underset{B}{[R_3B\cdot Me_3SiOOR''\cdot M]}$$

$$B \rightarrow RM^{\bullet} + Me_3SiO^{\bullet} + R''OBR_2$$

The formation of complex A and the radicals was confirmed by ESR. It is evident from the above scheme that formation of the complex (A) between the borane and peroxide takes place first, followed by the formation of ternary complex (B), by the addition of monomer to the complex A. The kinetics study[41b] supports this mechanism. Thus, according to Dodonov et al.,[41] only those monomers which can form a complex of type B could undergo polymerization under the specified conditions. It was observed[41] that although monomers like styrene or acrylates can easily generate the radicals as depicted above, esters of aliphatic carboxylic acids fail to do so. In addition, olefinic hydrocarbons like butene were not found to generate radicals by the above path for some unexplained reason. It was concluded[41] that compounds containing functional groups attached to α-position of the double bond only could generate the radicals. Acrylonitrile could not be polymerized since it formed a stable complex with the borane itself. A similar three-component intermediate complex also forms in the case of $R''_3MOOCMe_3$–R_3B (M = Si, Sn, Sb) catalyzed MMA polymerization.[42]

In light of the above study of Dodonov et al.,[41] we believe that a three-component complex is involved in the initiation step of R_3B–O_2-catalyzed reactions. The rate of reaction of R_3B with its peroxide derivative is too fast to allow the detection of any intermediate complex between them. Under circumstances, following indirect evidence provides support for the above hypothesis: (i) complex formation between benzoyl peroxide (BP) and R_3B has been proposed,[43] which lends support to the formation of complex of type A and (ii) Bu_3B and olefinic double bond of α,α-diphenylethylene form[44] a complex in ethanol (using the oxygen lone pair). This then suggests that R_3B and vinyl monomers can form a complex of type B in the presence of oxygen. It is worth mentioning that Davies[40] has proposed the formation of a complex between the monomer and boron peroxide instead of the trialkylborane.

The picture is clearer in the case of aluminum alkyl–acyl peroxide initiated polymerizations. A three-component complex formation mechanism is valid in this case, too.[25]

$$Al_2(C_2H_5)_6 + 2M \xrightarrow{\text{fast}} 2Al(C_2H_5)_3M \quad (18)$$

$$Al(C_2H_5)_3M + BP \xrightarrow{\text{slow}} [M\text{–}Al(C_2H_5)_3\text{–}BP] \quad (19)$$

$$[M\text{–}Al(C_2H_5)_3\text{–}BP] \rightarrow C_2H_5 + C_6H_5COOAl(C_2H_5)_2 + C_6H_5COOM^{\bullet} \quad (20)$$

It may be noted that BP by itself does not initiate polymerization by its dissociation due to the low reaction temperatures involved. Furthermore, Et_3Al and BP form a 2:1 complex in the absence of monomers, but not in their presence. Diethylaluminum benzoate and gaseous compounds derived from various reactions of ethyl radicals have been detected,[25] thus supporting the above scheme. Also, the following rate expression commensurate with the above mechanism was found valid in MMA, acrylonitrile, and vinyl acetate polymerizations:

$$R_p = k[M]^n[Al(C_2H_5)_3]^{1/2}[BP]^{1/2} \qquad (n > 1) \quad (21)$$

In the case of styrene and vinyl chloride, which cannot coordinate with aluminum alkyl, the polymerization could be initiated in the presence of complexing agents possessing ester or ether groups or acetonitrile.[25]

The chain transfer to trialkylboranes has been recently discovered by Ivanchev et al.[45] They found that if poly(vinyl acetate), prepared at 20 °C with R_3B–oxygen as initiator, is heated to 55 °C a high molecular weight polymer is obtained. In addition, saponification studies showed that the degree of branching for the polymer prepared at 55 °C is significantly larger than for the polymer prepared at 20 °C. They proposed that the propagating radicals ($P_n^{\bullet}$) react with the oxygen dissolved in the monomer to form a peroxide radical.

$$P_n^{\bullet} + O_2 \rightarrow P_nO_2^{\bullet} \quad (22)$$

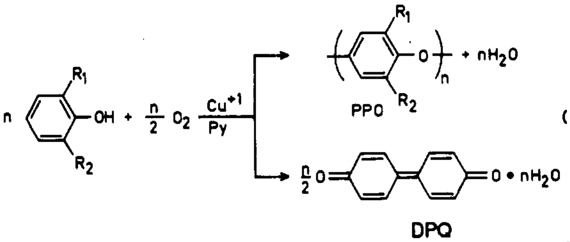
$$P_nO_2^{\bullet} + R_3B \rightarrow P_nOOBR_2 + R^{\bullet} \quad (23)$$

This radical reacts with trialkylborane to form organic boroperoxide, which is stable only at low temperatures.

The boroperoxide breaks apart at high temperature to initiate further polymerization, yielding a high molecular weight polymer. Since the polymer so obtained at high temperature would contain $-CH_2CH(Ac)$-$OCH_2CH(Ac)-$ type linkages (where Ac = acetyl group), they would yield, upon saponification, two molecules. This explains the observed increase in the degree of branching of the polymer obtained at 55 °C. Since R_3B is proposed to react with the $P_nO_2^{\bullet}$ radical, the corresponding reaction of its peroxide may also be possible. It may be worth studying the efficiency of boron peroxides as chain-transfer agents in this reaction, since their organic counterparts are known[46] to possess significant chain-transfer activity in radical polymerization. Razuvaev et al.[47] have also reported the chain-transfer activity of R_3B during MMA polymerization. The telechelic polymers bearing the boroperoxide end groups can be used for block copolymerization just as the hydroperoxide-terminated polystyrene (see section II.A.5), though no such study has been reported yet.

3. Oxidative Coupling of Phenols

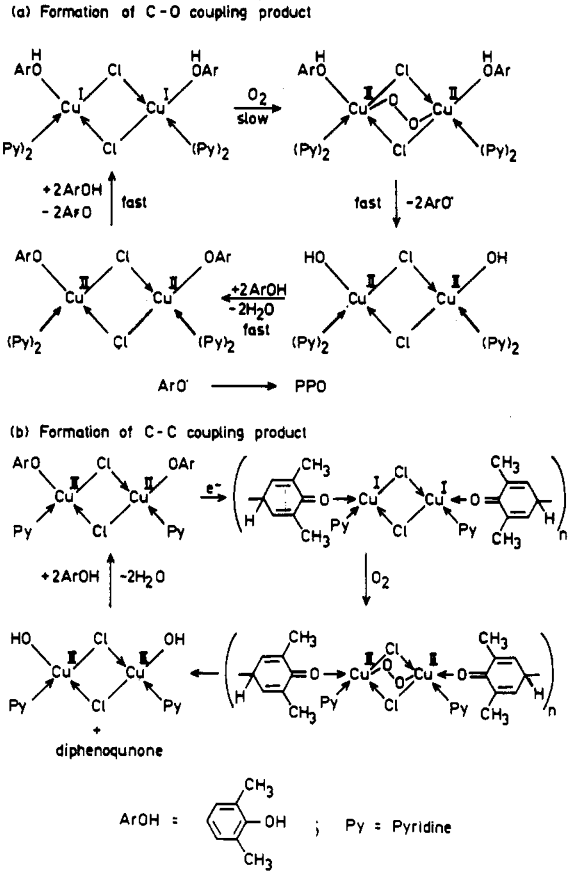
Various ortho-substituted phenols are known to undergo oxidative addition reactions to yield poly(phenylene oxide)s [PPO] in the presence of oxygen, Cu^{+1} salts, and some amines. The reaction is given as



(24)

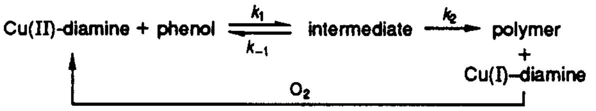
This reaction was first discovered by Hay et al.,[48] in 1959. It has been established that, when the substituents are small, the preferential pathway is the PPO formation. If one of the substituents is very large, such as a *tert*-butyl group, or if both are as large as isopropyl, then the formation of DPQ is favored. If the R's are electron-withdrawing substituents, it is very difficult to polymerize the phenols. The PPO is often termed as the C–O coupling product and quinones as the C–C coupling product. The other conditions which favor the C–O coupling product are low reaction temperature, high Cu–phenol ratio, and high amine–Cu ratio. However, Viersen and Challa[49] observed that even under the conditions most favorable for PPO, formation of DPQ (~3%) cannot be completely avoided and most of the DPQ is formed in the very beginning of the reaction. The Cu^{+1} salts or complexes in which metal is bound to the weaker ligands, like halides, are the most commonly used catalysts of this reaction. Copper(II) salts in pyridine (py) have been found to be inactive as catalysts for this reaction except for Cu(II) carboxylates which are considerably less reactive. Copper chelates, in which strongly chelating ligands like 8-hydroxyquinoline or ethylenediamine are present, do not catalyze this reaction. It is observed,[50] however, that dimeric $[LCuCl_2]_2$ where L is *N,N,N,N*-tetraethylenediamine, catalyzes the C–O coupling reaction. More recently, Tsuruya et al.[51] discovered that a catalyst system $CuCl_2$–KOH is active for the oxidative coupling of the phenols even in the absence of organic amines like pyridine. The activity and selectivity of this catalyst with respect to the C–C and C–O coupling modes has not yet been optimized.[52] Hence it is difficult to compare the efficacy of this catalyst with that discovered by Hay et al.[48] Other salts like AgO, PbO_2, etc. are also known[53] to catalyze this reaction. Another important characteristic of this reaction is that the molecular weight–conversion plot corresponds neither to chain growth nor to step growth propagation mechanisms. It is considered to exemplify the rare case of reactive intermediate condensation reactions.[54] Scheme I depicts the simplest representation of the C–O and C–C coupling modes for the reaction employing Cu^{1+}–pyridine catalyst as proposed by Price et al.[55]

SCHEME I. Mechanism of Phenolic Coupling Reaction



Apparently two different approaches can be recognized regarding the elucidation of the role of oxygen in this reaction: (i) kinetic studies of the reaction and (ii) analytical studies on the structure of the catalyst.

a. Kinetic Studies. Detailed studies on the kinetics of homogeneous polymerization were carried out by Tsuchida et al.[56] at constant partial pressure of oxygen. They proposed the following Michelis–Menten type kinetic scheme, wherein oxygen is involved in the reoxidation of Cu(I) to Cu(II), which, like the enzyme, is recycled in the reaction



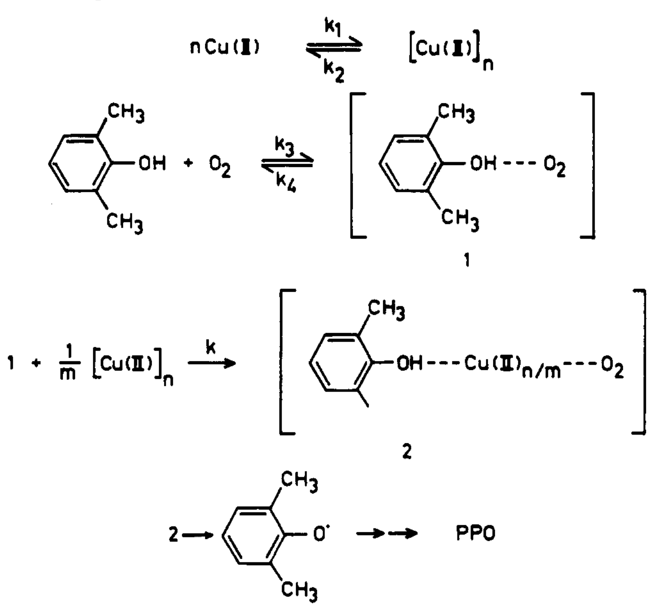
(25)

The rate expression for oxidative polymerization of phenols using this scheme was given[56] as

$$\text{rate} = k_2[\text{Cu}^{1+}]_0[\text{XOH}]/(k_m + [\text{XOH}]) \quad (26)$$

where [XOH] and $[Cu^{+1}]_0$ represent the concentrations of phenol and copper catalyst, respectively. Also, $k_m = (k_{-1} + k_2)/k_1$. Although this scheme in principle, is well founded for oxidative coupling of phenols, Mobley[57] found that 26 is valid only for one cycle of the catalyst operation, because it gets deactivated during subsequent recycling. Mobley[57] also realized that during this stepwise polymerization reaction of phenols, the reactivity of the monomer is significantly different than the oligomers, unlike for typical polycondensation reactions. This is consistent with the reactive intermediate condensation character proposed for this polym-

SCHEME II. Heterogeneously Catalyzed Phenolic Coupling Reaction



erization.[54] He, therefore, modified the earlier scheme of Tsuchida et al.[56] as follows:

$$\text{rate} = \frac{[k_{21}(1-p) + k_{2n}][\mathrm{Cu}^{1+}]_0 e^{-k_3 t}[\mathrm{XOH}]}{1/k_1 + [\mathrm{XOH}]} \tag{27}$$

where k_{21} and k_{2n} represent the rate constants for the monomer and oligomer formation, respectively, k_3 is the rate constant for catalyst deactivation, n stands for the degree of polymerization, and p is the extent of reaction at time t. $[O_2]$ is not directly considered in this reaction but it can be indirectly expressed since its stoichiometric relation with [XOH] is known (as given in eq 24). Experimental results obtained over several cycles of catalyzed reaction showed that both the above assumptions are valid, and good agreement between the model and experimental data was observed.[57]

The rate expression 28 has been proposed by Tsuruya et al.[51] for the heterogeneously catalyzed phenolic coupling reaction of 2,6-dimethylphenol using $CuCl_2$–KOH catalyst (also see Scheme II). Under the condition k_4

$$\text{rate} = \frac{k k_3 k_1^{1/m}[\mathrm{O_2}][\mathrm{Cu}^{2+}]^{n/m}[\mathrm{XOH}]}{k_4 + k k_1^{1/m}[\mathrm{Cu}^{2+}]^{n/m}} \tag{28}$$

$\gg k k_1^{1/m}[\mathrm{Cu}^{2+}]^{n/m}$, the rate will be first order in the concentration of XOH and oxygen while it can have a fractional order with respect to Cu(II) (if $m > n$). Experimentally, at low concentration of $CuCl_2$, the rate was found to vary with 0.5 order with respect to $CuCl_2$. At higher concentrations of $CuCl_2$, k_4 may be neglected and then, according to eq 28 the rate would be independent of $CuCl_2$ concentration, concurrent with the observation.

It is clear from the foregoing discussion that kinetic studies of the homogeneously catalyzed reaction support the overall stoichiometry of the reaction (eq 24). Apart from explaining the role of Cu as a catalyst, these studies also account for the differences in the reactivity of the various oligomeric species. However, these kinetic studies[56-58] are insufficient to describe the role of oxygen in C–O coupling reaction in that oxygen is assumed to be used only in the reoxidation of Cu(I). However, recent studies[49] have proved that the homogeneous phenolic coupling reaction catalyzed by the Cu^{1+}–amine–oxygen system is a very complicated redox process involving four electron-transfer steps. The reaction catalyst itself is polymeric in nature, and it contains oxygen in each repeat unit. Further, Davies et al.[59] showed that metamorphosis of the initial Cu^{1+} salt into the polymeric catalyst via dimeric and tetrameric species can be detected by the controlled addition of amine. Since the stoichiometry of this multistep metamorphosis is difficult to study, any kinetic study, particularly with respect to the rate of consumption of oxygen, may not give[60] meaningful information regarding the structure of the polymeric catalyst containing oxygen. It is more difficult to comprehend the case of heterogeneously catalyzed reaction since oxygen is considered to play an additional role in the dissolution of the heterogeneous catalyst.

b. Analytical Studies on Catalyst Structure. One of the early attempts to understand the structure of active catalyst of the phenolic coupling reaction was made by Coudurier et al.[61] They found that the stoichiometry of the active catalyst Cu–pyridine–O_2 is 1:1:0.5, indicating that oxygen is an integral part of the active catalyst. Cu–O–Cu bridges (absorption peak at 575 cm^{-1}) were inferred from the IR study and were thought to be active during polymerization.

Although the exact nature of the Cu–O interaction was not very clear from this study, Kramer et al.[62] speculated it to be peroxidic linkages although they were aware that peroxides of low-valent Cu were not known at that time. Khlebnikov et al.[63] also supported this view and, while reporting the stoichiometry of the catalyst Cu^{1+}–Cu^{2+}–O_2 as 3:2:1, they proposed the following structure:

$$(\mathrm{Cu^+{-}Cl^-{-}Cu^{2+}Cl^-{—}O_2^{2-}{—}Cu^+Cl^-{-}Cu^+Cl^-})(\mathrm{Py})_n$$

In the subsequent studies, Bodek and Davies[64] found that the catalyst could be obtained by the following stoichiometric reaction:

$$4\mathrm{CuCl} + \mathrm{O_2} \xrightarrow{\text{pyridine}} \underset{\mathrm{A}}{2(\mathrm{py})_2\mathrm{CuCl_2}} + \underset{\mathrm{B}}{2[(\mathrm{py})_m\mathrm{CuO}]_n} \tag{29}$$

A was found to be a simple Cu(II) complex, green in color and catalytically inactive. However, B was found to yield a brown solution in pyridine and contained Cu-py in varied ratios ranging from 1:0.5 to 1:4, depending upon the pyridine concentration. The B component was catalytically active and could be separated from component A by passing the mixture over a GPC column. Bodek and Davies[64] thus discovered that the active catalyst (B) is polymeric in nature. The activity of B however, was observed only in solution. Attempts to isolate the polymeric catalyst in the form of a stable solid either by evaporating the solvent or by complexing with ligands, like 2,9-dimethyl-1,10-phenanthroline, were unsuccessful.[64] This polymeric catalyst undergoes further polymerization upon heating which explains the observed induction period during oxidative polymerization experiments at higher temperatures.[64] Each repeat unit of the polymeric catalyst contains more of pyridine molecules than Cu. This may be the reason for high ratios of amine–Cu favoring C–O coupling reaction.

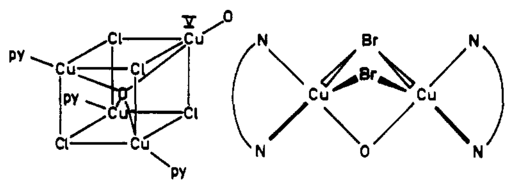


Figure 1. Schematic representation of copper catalysts of the phenolic coupling reaction: (a) tetranuclear oxocopper(II) complex and (b) binuclear copper(II) complex.

There is some evidence that structure of the catalyst containing oxygen can be significantly altered by the nature of ligands coordinated with the Cu center. In the case of $[LCuCl_2]_2$ dimer mentioned earlier for example, oxygen is found to oxidize the Cu^{1+} complex to peroxocopper species which is a catalyst of C–O coupling reaction.[64] On the other hand, it appears[60] that this polymeric catalyst may not contain peroxy-linked copper, as thought earlier,[64] since the formation of peroxocopper(II) species is not favored with pyridine ligand.

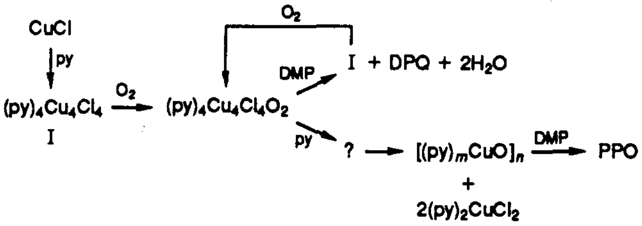
Meinders et al.[65] found that a copper complex synthesized from CuCl and *N,N,N′,N′*-tetramethylethane-1,2-diamine is an active catalyst for the phenolic coupling reaction. From spectroscopic and X-ray studies of this complex, they showed that this catalyst is active only if it contains bridging hydroxyl ligands (μ-hydroxo ligands). A similar effect of the OH^- ions on the catalytic activity was observed for the homogeneous catalyst obtained from soluble Cu complexes with poly[styryl-(4-vinylpyridine)] and poly[styrene-*N*-vinylimidazole] copolymers.[65]

It appears from the above discussion that the structure of Cu–py–O_2 containing catalyst has yet to be established except for the fact that the catalyst is polymeric in nature. Also, the structure of the active catalysts of this reaction is strongly dependent on the type of amino ligands attached to the Cu compound.

In order to understand the structure of the catalytic species formed in the phenolic coupling reaction, Davies and co-workers[66-68] have studied the oxidation of various halo(amine)Cu^{1+} complexes. Although the primary oxidation products of such reactions was found to be either dimeric[66] or tetrameric,[67] they could not be isolated as stable solids. The spectroscopic and cryoscopic studies, however, established that dimers and tetramers have the formulas $L_2Cu_2X_2O$ and $L_4Cu_4X_4O_2$, respectively, (L = ligands like pyridine, X = halogens). The proposed schematic structures of these species are given in Figure 1. These compounds react with excess amine to form the polymeric catalysts, yielding PPO instead of DPQ.[66,67]

These multinuclear oxidation products are usually prone to disproportionation in air, but in one case[69] even the disproportionation product was found to retain the catalytic activity. Fortunately, it could be isolated in crystalline form; X-ray study indicated that this catalyst, $[(nmp)_3Cu_4OCl_6(O_2H\cdots nmp)$, nmp = *N*-methyl-2-pyrrolidone], has a "beryllium acetate" core of T_d geometry (Figure 2). Thus, this catalyst possesses one Cu center distinctly different from the other centers in that it is attached to an "aquo" ligand.

In more recent work, Davies et al.[58] have reported the kinetic evidence for the catalytic activity of the tetranuclear $(py)_3Cu_4Cl_4O_2$ complex (schematically represented in Figure 1, part a) in the C–C coupling reaction of 2,6-dimethylphenol (DMP). The precursor of this complex namely, the tetranuclear complex $(py)_4Cu_4Cl_4O_2$, is also found to catalyze this reaction. Davies et al.[58] believe that during the phenolic coupling reaction phenolic substrate attacks the site V bearing the terminal oxo group (see Figure 1, part a) thus yielding an intermediate Cu(II) complex which carries one phenolate and one hydroxo group at site V. Simultaneously, the copper center at site V changes its coordination number from 5 to 6 to become ESR active. Given below is the schematic summary of the present status of the process:



In the case of the $CuCl_2$–KOH heterogeneous catalyst system, Tsuruya et al.[51] found that a solid precipitates from the reaction mixture of $CuCl_2$ and KOH, which appears to be a polynuclear Cu complex. It is observed[51] that this solid remains insoluble in benzene even in the presence of oxygen and the substrate, and no reaction takes place under this condition. On the other hand, the same solid complex slowly dissolves in methanol iin presence of oxygen and the substrate. On the basis of the ESR study of the active copper catalyst present in the solution, it is considered[52] to have the

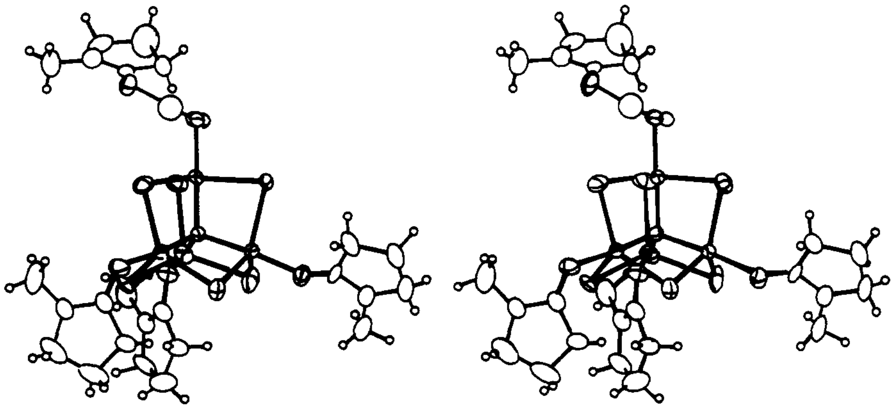
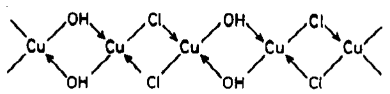


Figure 2. Stereoscopic view of the $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecule.

following structure:



However, the role of oxygen in the formation of the active, homogenized catalyst is difficult to envisage from this study.

4. Redox Initiation Using Oxygen

Oxygen promotes the redox initiated polymerization processes in one of the following ways:

(i) Oxygen can participate in an extra initiation reaction to increase the rate of initiation and hence the yield of polymer. For example, Narain et al.[70] concluded that oxygen acts as a cocatalyst for the ascorbic acid (AH_2)–peroxydisulfate-initiated polymerization of acrylamide since large induction periods were observed under deaerated conditions. They suggested that in addition to the expected redox reaction between the oxidant and reductant, an extra redox reaction takes place between oxygen and ascorbic acid to produce the radical $AH^{\bullet}$ as follows:

$$AH_2 \xrightarrow[O_2]{\text{slow}} AH^{\bullet} + HO_2 \tag{30}$$

where A is the reduced form of ascorbic acid. The $AH^{\bullet}$ itself can itself initiate the polymerization or it can also react with peroxydisulfate to produce the primary radical ($SO_4^{\bullet-}$), which is actually produced by the redox reaction

$$AH^{\bullet} + S_2O_8^{2-} \rightarrow A + SO_4^{2-} + SO_4^{\bullet-} + H^+ \tag{31}$$

Other redox reactions[71-75] involving autooxidizable reactants like hydrazine hydrate[71] or sulfite ion[72] also exhibit similar behavior.

(ii) Oxygen can reoxidize the reduced oxidant which can be recycled for the additional production of radicals. For example, Menon and Kapur[76] observed that redox reaction between $CuSO_4$ and hydrazine generates primary radicals besides the Cu^{1+} species. This Cu^{1+} species can be reoxidized to Cu^{2+} by oxygen, which then recycles in the redox reaction.

(iii) Oxygen can itself participate in a redox reaction to generate the initiating radicals. For example, Reddy et al. reported[77-79] the polymerization of various vinyl monomers in the presence of oxygen, ascorbic acid and transition metal salts (M^{n+}). The initiation is proposed to involve the formation of a complex intermediate as shown below:

$$AH_2 + O_2 + M^{n+} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k} R^{\bullet} \tag{32}$$

The redox reaction between AH_2 and M^{n+} can take place even in the absence of oxygen. However, the rate of polymerization of such reaction is many fold lower than in the presence of oxygen. The kinetic data[77] in the case of Cu^{2+} indicated that the rate of polymerization increased with $[O_2]$ up to 6.5×10^{-4} M and thereafter remained constant. The order with respect to $[O_2]$ was 0.5 at low $[Cu^{2+}]$. At high $[Cu^{2+}]$, the order was higher (0.7). The kinetic model proposed to account for these observations is consistent with the view that oxygen participates in the initiation reaction. However, no independent evidence for the structure of oxygen containing complex has been presented so far; the complex formation is propounded only on the basis of the proposed kinetics scheme.[80]

In many photosensitized polymerization reactions the presence of oxygen has been found to be mandatory.[81] An essential feature of these systems is the reduction of the excited sensitizer molecule (commonly a dye, denoted as S in the following equations) by a mild reducing agent. The reduced species (RH) so formed reacts with either oxygen or a radical derived from the reduction of oxygen with the reducing agent ($O_2H^{\bullet}$) to produce hydrogen peroxide. Simultaneously, the sensitizer (S) is also regenerated. Primary radicals ($R''^{\bullet}$) are formed by the following redox reaction of the reducing agent with hydrogen peroxide:

$$S \xrightarrow{h\nu} R^{\bullet} \tag{33}$$

$$R^{\bullet} + \text{reducing agent} \rightarrow RH \tag{34}$$

$$RH + O_2(O_2H^{\bullet}) \rightarrow R'^{\bullet} + O_2H^{\bullet}(H_2O_2) \tag{35}$$

$$R'^{\bullet} + O_2(O_2H^{\bullet}) \rightarrow S + O_2H^{\bullet}(H_2O_2) \tag{36}$$

$$H_2O_2 + \text{reducing agent} \rightarrow R''^{\bullet} \tag{37}$$

For explaining the kinetics of such processes, however, the initiation step is considered to be a concerted reaction involving all the above steps, i.e., in the kinetic scheme given in eqs 38–42, the initiator includes simultaneously the sensitizer, the reducing agent, and oxygen.

$$\text{initiation} \qquad \text{initiator} + \text{monomer} \xrightarrow[h\nu]{k_i} R''^{\bullet} \tag{38}$$

$$\text{activation} \qquad \text{monomer} + R''^{\bullet} \xrightarrow{k_a} R''M^{\bullet} \tag{39}$$

$$\text{propagation} \qquad R''M^{\bullet} + nM \xrightarrow{k_p} P_n^{\bullet} \tag{40}$$

$$\text{termination} \qquad 2P_n^{\bullet} \xrightarrow{k_t} P \tag{41}$$

$$\text{cage recombination} \qquad 2R^{\bullet} \xrightarrow{k_5} S \tag{42}$$

Assuming a steady state, the rate of polymerization is given by

$$R_p = k_p[M]\left[\frac{k_i k_a[\text{initiator}][M]^2}{(k_a[M] + k_5)}\right]^{1/2} \tag{43}$$

Since experimentally R_p was found to depend on $[M]^2$, it was concluded[81] that cage recombination of primary radicals was very significant in this case, implying

$$R_p \propto [O_2]^{1/2}[S]^{1/2}[\text{reducing agent}]^{1/2}[M]^2$$

which was observed in certain concentration ranges of each of these species. Although no polymerization took place in the complete absence of oxygen, a significant induction period was noticed at higher oxygen concentrations.

Tanaka[82] has reported an interesting redox system based on $TiCl_3$ and oxygen, confirmiing the absence of polymerization of MMA in oxygen-free atmosphere.

Most of the above studies give only a qualitative picture of various roles of oxygen in redox polymerization. The supporting kinetic evidence has not been acquired in many cases and even crucial information, like the structure of complex formed between AH_2, oxygen and M^{n+} is lacking.

TABLE II. Oxidation Products of Poly(styryl)lithium[a]

method of estimation[b]	M_n	solvent	coupling, %	PSO_2PS, %
1	18000	benzene	21	–
2			18	3
3			19	2
1	18000	benzene–THF (75/25)	36	
2			21	15
3			22	14
1	4200	benzene	28	
2			20	8
3			18	10
1	4200	benzene–TMEDA (500/1)	36	
2			19	17
3			18	18

[a] Reference 76. [b] Numbers represent the following: 1, amount of dimeric product determined by GPC; 2, amount of PSO_2PS estimated by reduction with lithium aluminum hydride; 3, amount of PSO_2PS estimated by degrading it by heating at reflux in toluene and finding out the reduction in dimer content by GPC.

5. Effect of Oxygen on Anionically Terminated Polymers

Even in the early days of anionic polymerization chemistry, oxygen was known to increase the viscosity of solution containing living polymers.[83] However, no serious attention was paid to study the reaction of such an "adventitious" impurity because the characteristic "living nature" of the process was a more hotly pursued topic. The main work on the effect of oxygen on anionic chain ends has been carried out only in past few years.

Fetters and Firer[84] observed that the use of polar additives or solvents resulted in the formation of a greater fraction (up to 40%) of the coupled material on aerial termination, compared to aerial termination in hydrocarbon media. Soon after this report, Mansson[85] tried to identify the products of the reaction of polystyryllithium with molecular oxygen. Though alcohol and ketone chain end functionalized products were detected, they are believed[86] to have formed during the work-up procedures employed. The first quantitative study on the reaction of polystyryllithium and molecular oxygen has been reported by Catala et al.[87] They studied the influence of a variety of reaction conditions on the course of oxidation of polystyryllithium and found that a coupling product (a dimer formed from two original living polymer chains) and a hydroperoxide-terminated polystyrene (PSO_2H) are the resultant products of this reaction. Furthermore, the ratio of these two products varies depending upon the reaction conditions. For instance, in the oxidation carried out

$$\mathrm{PSLi} + \mathrm{O_2} \xrightarrow[\text{addition}]{\text{inverse}} \text{dimer } (9\%) + \mathrm{PSO_2H}\ (91\%) \tag{44}$$

in THF at −65 °C, 20% dimer was formed while addition of the living polymer to an oxygen-saturated solution (inverse addition) yielded only 9% dimer. Also, the corresponding hydroperoxide functionality was obtained in 91% yield under these conditions. A similar result, i.e., efficient formation of the hydroperoxide, was obtained during a solid state oxidation reaction.

Quirk et al.[86,88] carried out a detailed investigation of the oxidation of polystyryllithium in polar and nonpolar solvents and have proposed the following scheme for the oxidation reaction of polystyryllithium:

$$\mathrm{PSLi} + \mathrm{O_2} \rightarrow \mathrm{PS^\bullet} + \mathrm{Li^+O_2^-} \tag{45}$$

$$\mathrm{PS^\bullet} + \mathrm{O_2} \rightarrow \mathrm{PSO_2^\bullet} \tag{46}$$

$$\mathrm{PSO_2^\bullet} + \mathrm{PSLi} \rightarrow \mathrm{PSO_2Li} + \mathrm{PS^\bullet} \tag{47}$$

$$2\mathrm{PS^\bullet} \rightarrow \mathrm{(PS)_2}\ \text{(dimer)} \tag{48}$$

$$2\mathrm{PS^\bullet} \rightarrow \mathrm{(PS)CH{=}CHPh} + \mathrm{(PS)CH_2CH_2Ph} \tag{49}$$

$$\mathrm{PS^\bullet} + \mathrm{PSO_2^\bullet} \rightarrow \mathrm{PSO_2PS} \tag{50}$$

$$2\mathrm{PSO_2^\bullet} \rightarrow [\mathrm{PSO_4PS}] \rightarrow {}^1\mathrm{O_2} + \mathrm{(PS)CH_2C(O)Ph} + \mathrm{(PS)CH_2CH(OH)Ph} \tag{51}$$

$$\mathrm{PS^\bullet} + \underset{\text{(solvent)}}{\mathrm{RH}} \rightarrow \mathrm{PSH} + \mathrm{R^\bullet} \tag{52}$$

The overall reaction is given as

$$\mathrm{PSLi} \xrightarrow[\text{(2) } \mathrm{H_2O}]{\text{(1) } \mathrm{O_2}} \mathrm{PSH} + \mathrm{(PS)_2} + \mathrm{PSO_2PS} + \mathrm{PSO_2H} + \mathrm{(PS)CH_2C(O)Ph} + \mathrm{(PS)CH{=}CHPh} + \mathrm{(PS)CH_2CH(OH)Ph} \tag{53}$$

The formation of all these products is not yet conclusively proved; Catala et al.[87] have found some evidence for the hydroperoxide formation and a macroperoxide (PSO_2PS) has been reported by Quirk and Chen.[88] They also found that PSO_2PS accounts for approximately 50% of the dimer product in the presence of Lewis bases like TMEDA (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine) and THF (Table II). Further, it was observed that though the Lewis acids lead to a decrease in PSO_2H content, almost 95% PSO_2H could be obtained by solid-state oxidation of polystyryllithium by freeze drying the benzene solution of the polymer (Table III). This result comports the earlier report of Catala et al.[87]

The only drawback in this study is the lack of information regarding the structure of nonperoxidic products (POH), which is the major product of this oxidation reaction in liquid state (Table III). Nevertheless, the importance of synthesizing such a peroxide end group possessing oligomers lies in their potential applications in block copolymerization,[86] and they can also be used perhaps for the "multicomponent polymerization", proposed by Eastmond.[89] In this

TABLE III. Oxidation Products of Polystyryllithium[a]

oxidation condition	molecular weight	solvent	yield, wt %			
			$(PS)_2$	PSO_2-PS[b]	PSO_2H[c]	P-OH[d]
liquid state	18000	benzene	19	3	9	69
		benzene–THF (75/25)	22	15	5	58
	4200	benzene	19	9	5	67
		benzene–THF (75/25)	19	18	2	61
		benzene–TMEDA[e]	18	14	3	67
solid state	4200	–	4	1	95	–

[a] Reference 76. [b] From $LiAlH_4$ reduction and thermal decomposition. [c] From iodometric titration. [d] POH represents the amount of nonperoxidic, nondimerized products. [e] PSLi and TMEDA taken in 1:1 molar ratio.

context, therefore, similar studies on the anionic polymerization of other vinyl monomers could be rewarding.

B. Assorted Studies

Uehara[90] reported a systematic kinetics study of MMA polymerization, using *p*-toluenesulfinic acid (TSA) in the presence of oxygen and some oxygen acceptor like *N*,*N*-dimethylaniline (DMA), based on an earlier report by Hagger.[91] Uehara observed that TSA as such fails to initiate the polymerization of MMA. The kinetics[90] of the reaction suggests

$$R_p = k[O_2][TSA]^{1/2}[DMA]^{1/2}[MMA]^{1/2} \qquad (54)$$

Formation of a salt between TSA and DMA is speculated to take place, followed by its reaction with oxygen to generate the initiating radicals.

Wang et al.[92] have studied the effect of combining photosensitized polymerization with the well-known peroxide–amine-based initiation. For MMA polymerization, they used the system benzophenone–triethylamine–oxygen. The combination of benzophenone and light produces peroxy radicals in the presence of oxygen which can be efficiently decomposed by the amine, producing the primary radicals. The rate of oxygenation was first order for benzophenone concentration and 0.8 order for triethylamine concentration. Carboxylic acid[93,94] additives were found to promote this polymerization. Further, Wang et al.[95] reported that the low experimental value of $[k_p/(k_t)^{1/2}]$ agrees with the termination by a primary radical (k_p and k_t are the propagation and termination rate constants, respectively). Vila et al.[95] observed that when MMA is polymerized under the varying oxygen pressure (in the range 10–60 cm), the following linear equation holds:

$$\log (R_p/R_t) = (3.7 \pm 0.6) - [(9200 \pm 800)/4.6T] \qquad (55)$$

where R_t is the rate of termination.

The determination of reactivity ratios of comonomers is one of the important aspects of the study of copolymerization. It is interesting to know whether oxygen can influence the reactivity ratios since this may bring about changes in the chemical composition of the copolymer formed and can certainly influence the copolymer properties. Zabotin et al.[96] found that the composition of the copolymer of butyl acrylate and acrylonitrile (containing about 50% acrylonitrile) was not affected by the atmospheric oxygen. On the other hand Ivanchev et al.[97] reported an interesting observation—during the emulsion copolymerization of vinyl acetate (M_1) and butyl acrylate (M_2), the reactivity ratios were $r_1 = 0.67$ and $r_2 = 0.91$ in deaerated water while in aerated water they changed to $r_1 = 0.074$ and $r_2 = 4.89$. Thus the acrylate content of the copolymer increased substantially in the presence of aerial oxygen. Although the exact reasons for such significant changes are unknown, it was suggested that oxygen has perhaps attached itself to emulsified monomer particles in amounts which differed for the two monomers.

Poly(phenylene oxides) can also be synthesized by displacement of halogen from a 4-halo-2,6-disubstituted phenol in the presence of a base (e.g. NaOH) and a catalytic amount of initiator. Unlike oxidative polymerization of phenols which requires a stoichiometric amount of oxidizing agent, the displacement polymerization requires only a catalytic amount of an oxidizing agent as an initiator. Shaffer and Percec[98] have recently reported the displacement polymerization of 4-bromo-2,6-dimethylphenol under phase-transfer condition wherein aerial oxygen plays the role of an oxidizer.

Kovacic and co-workers[99] have studied the Friedel–Crafts polymerization of several aromatic compounds to corresponding polyarylenes. Particularly in the system $AlCl_3$–$CuCl_2$ and benzene, they have found convincing evidence for a cationic, stair-step propagation mechanism. In one of their reports,[100] it was found that polyphenylene is also formed during polymerization of benzene catalyzed by $AlCl_3$ alone. This reaction appears to be interesting because it does not yield a polymer under inert conditions, like conventional Friedel–Crafts polymerizations. On the other hand, polymerization takes place in dry air, and also in the oxygen atmosphere. Although the mechanism of this reaction is not yet confirmed, and it is speculated that traces of moisture may act as the cocatalyst. The role of oxygen in this reaction may prove to be interesting, because usually the cationic intermediates are stable only in an inert atmosphere.

III. Role of Oxygen in Inhibition of Polymerization

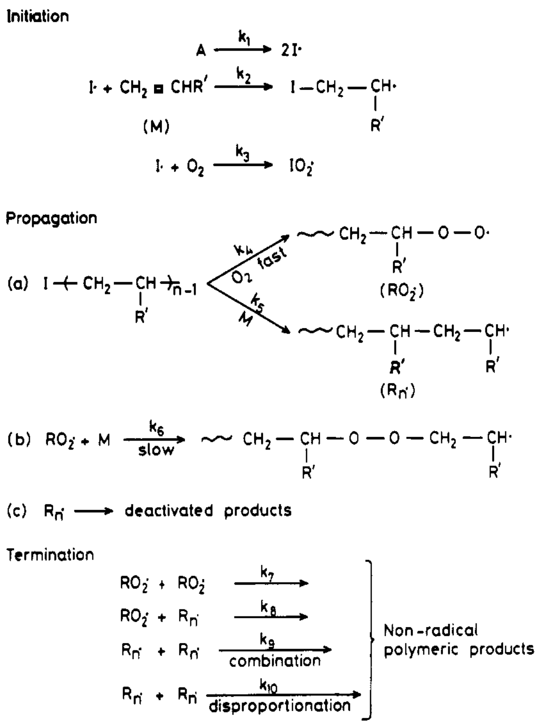
A. Study of Polyperoxides

Compared to ionic and other types of polymerization reactions, more is known about the inhibitory action of oxygen in radical polymerization reactions. Notwithstanding early controversies regarding the role of oxygen in radical polymerization (which have been reviewed by Bovey and Kolthoff[16]), it is now well established[6,101] that oxygen forms an alternate copolymer with a vinyl monomer (called polymeric peroxide or polyperoxide) in a reaction which competes with the usual propagation reaction to bring about the inhibition of polymerization.

Understandably, because of the presence of thermally labile peroxidic linkages, these polyperoxides decompose at higher temperatures (usually about 100–150 °C) to produce free radicals capable of initiating polymerization.[6] This has been strongly supported by the recent quantitative studies reported from this laboratory,[102,103] which prove that breakage of the peroxidic linkage is the primary step in the thermal degradation of polyperoxides. The inhibitory action of oxygen is thus unique in the sense that even during the induction period a polymerization reaction takes place to yield a thermally unstable polyperoxide. *The inhibitory action of oxygen in radical polymerization is, therefore, not permanent and strongly depends upon the temperature.*

Mayo et al.[104] showed that whereas the autooxidation of hydrocarbons containing relatively unreactive double bonds yield alkyl hydroperoxides, hydrocarbons containing reactive double bonds (e.g. vinyl monomers) simultaneously form polyperoxides under these conditions. The product ratio (hydroperoxide–polyperoxide) in the overall yield varies with oxygen pressure although they are formed through a common intermediate. Subsequent studies by Mayo et al.[105] proved that the autooxidation of vinyl monomers at oxygen partial pressure of about 1 atm and above can be quantitatively

SCHEME III. Peroxide Scheme



interpreted by simply assuming that only the copolymerization reaction between a monomer and oxygen takes place during the oxidation (Scheme III). These studies[104,105] also indicated that the reactivity ratio of vinyl monomers in this copolymerization reaction is very low (10^{-5}), implying that a typical vinyl monomer reacts many thousands time faster with oxygen than with itself at equal concentration of the two reactants. Further, the peroxide radical so formed reacts very slowly and hence in radical polymerization reactions carried out in the presence of even traces of oxygen, an induction period (τ) is always observed. To derive quantitative results on the effect of dissolved oxygen during polymerizations, Decker and Jenkins[106] studied the photopolymerization of multi-acrylate systems in air. As expected, they found that homopolymerization does not begin until all the dissolved oxygen forms the peroxide (because $k_4[O_2] \gg k_5[M]$, see Scheme III). Further, they found that the dissolved oxygen concentration has to decrease by a factor of about 250 for the homopolymerization to begin. The lower limit of oxygen concentration will be dictated, of course, by the polymerization rate and diffusion of oxygen.

Many investigators[107-111] have tried to correlate τ with experimental variables like the concentrations of the monomer, oxygen, and the initiator, assuming that polyperoxide is the only product of the oxygen-consumption reaction. They have used the peroxide scheme (Scheme III) to obtain the quantitative expressions. The general expression correlating with the experimental variables, obtained from such studies is

$$\tau = K[O_2]^a[M]^b[A]^c \tag{56}$$

The values of the exponents a, b, and c signify whether $R^\bullet$ terminates by combination or disproportionation (Scheme III) in a particular polymerization reaction under consideration. A general approach to arrive at a specific form of eq 56 is discussed below.

According to Schulz et al.[107] the τ is defined as

$$\tau = [O_2]_0/(-d[O_2]/dt) \tag{57}$$

where $[O_2]_0$ is the concentration of oxygen present in the system at the beginning of the polymerization and $(-d[O_2]/dt)$ represents the rate of consumption of oxygen or, in other words, the rate of oxidation of the monomer.

Recently, Garton and George[109] have reported a more general relation between τ and the relevant concentration terms. For this purpose, they introduced the following two assumptions in the general peroxidation model described in Scheme III: (i) the contribution of the side reaction c in the propagation step is negligible and (ii) each radical formation reaction reaches a steady state, thereby allowing to equate the rate of generation of free radicals to the rate of their consumption.

Using these assumptions and Scheme III following rate equation was derived:

$$fk_1[A] = (k_9 + k_{10})[R^\bullet]^2 + k_8[RO_2^\bullet][R^\bullet] + k_7[RO_2^\bullet]^2 \tag{58}$$

where f represents the initiator efficiency. Garton and George further assumed that a reasonably high molecular weight peroxide was formed during a significant induction period, which allows the following equality for the steady-state polyperoxidation:

$$k_4[R^\bullet][O_2] = k_6[RO_2^\bullet][M] \tag{59}$$

Substituting $[R^\bullet] = (k_6[M]/k_4[O_2])[RO_2^\bullet]$ into eq 58, we get

$$fK_1[A] = k'\left[\frac{k_6[M]}{k_4[O_2]}[RO_2^\bullet]\right]^2 + k_8\left[\frac{k_6[M]}{k_4[O_2]}\right][RO_2^\bullet][RO_2^\bullet] + k_7[RO_2^\bullet]^2 \tag{60}$$

where $k' = k_9 + k_{10}$.

Rearranging the above equation one obtains

$$[RO_2^\bullet] = \left[\frac{fk_1[A]}{k'\left(\frac{k_6[M]}{k_4[O_2]}\right)^2 + k_8\left(\frac{k_6[M]}{k_4[O_2]}\right) + k_7}\right]^{1/2} \tag{61}$$

The rate of consumption of oxygen is given by

$$-d[O_2]/dt = k_4[R^\bullet][O_2] = k_6[RO_2^\bullet][M] \tag{62}$$

Substitution of the value of $[RO_2^\bullet]$ from eq 61 into eq 62 yields

$$\frac{-d[O_2]}{dt} = k_6[M]\left[\frac{fk_1[A]}{k'\left(\frac{k_6[M]}{k_4[O_2]}\right)^2 + k_8\left(\frac{k_6[M]}{k_4[O_2]}\right) + k_7}\right]^{1/2} \tag{63}$$

Garton and George[109] were able to obtain the exponents a, b, and c of eq 56 using modified form of the above general eq 63 for the liquid-phase polymerization of vinyl chloride at 55 °C. Thus, if the cross termination reaction between the radicals $RO_2^\bullet$ and $R^\bullet$ is assumed to be predominant, eq 63 simplifies to

$$-d[O_2]/dt = (fk_1k_4k_6[M]/k_8)^{1/2}[A]^{1/2}[O_2]^{1/2} \tag{64}$$

Substituting for $d[O_2]/dt$ from eq 64 into eq 57, one obtains

$$\tau = \frac{[O_2]}{(fk_1k_4k_6[M]/k_8)^{1/2}[A]^{1/2}[O_2]^{1/2}}$$

or

$$\tau = k''[O_2]^{1/2}[M]^{-1/2}[A]^{-1/2} \qquad (65)$$

where $k'' = (fk_1k_4k_6/k_8)^{-1/2}$.

The values of $a = 1/2$ and $c = -1/2$ so obtained in eq 65 are consistent with those observed experimentally. On the other hand, in aqueous polymerization of acrylamide George and Ghosh[110] could correlate the experimental observation ($a = 1$, $b = c = -1$) only with the model involving unimolecular termination reaction: $RO_2^{\bullet} \rightarrow$ inactive product. They also felt that this was an incomprehensible result, requiring further attention.[110]

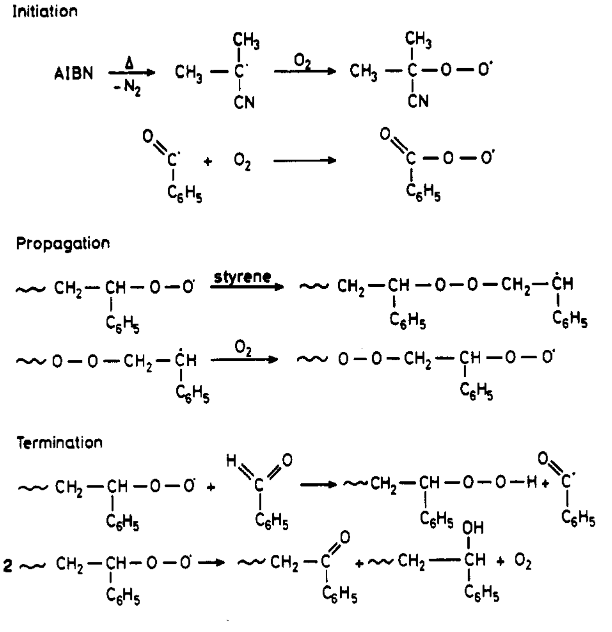
Mayo et al.[105] observed that results of Shulz et al.[107] and Henrici-Olive et al.[108] regarding the correlation of τ with various concentration terms during the autooxidation of styrene and MMA could not be explained on the basis of their copolymerization reaction model. This is because polyperoxide was assumed to be the only reaction product during the induction period preceding the polymerization. Mayo[105] further suggested that this disagreement may also arise because the rate constant of either the propagation or the termination step is not a suitable measure of the polyperoxidation reaction. Interestingly, theoretical calculations using a Schulz[107] or Henrici-Olive[108] scheme match well with the experimental results in more complex situation where extra inhibitor is present in addition to oxygen, leading to synergistic inhibition.[112,113]

All the above studies assumed a strictly alternating structure of the peroxide copolymer, and the reaction sequence depicted in Scheme III. However, the detailed NMR spectral analysis of polystyrene peroxide by Cais and Bovey[114] shows that polyperoxidation is actually a complicated process. They found that during a AIBN-initiated polyperoxidation of styrene (i) the initiating radicals are not the usual primary radicals obtained from AIBN decomposition, and (ii) the termination by bimolecular combination of the growing chains is not the major route. Instead, benzaldehyde, which is formed simultaneously with the peroxide, is considered to preferentially terminate the growing chains. The polymerization reaction proposed by Cais and Bovey[114] is summarized in Scheme IV. This alternate route for polyperoxidation has been proposed on the basis of the end-group analysis and the study of monomer sequence distribution using ^{13}C NMR.

In light of the above discussion we conclude that the peroxide scheme provides a reasonable qualitative explanation for the inhibitory action of oxygen in radical polymerization. The quantitative correlations are however lacking in many cases; further studies on termination reactions during the autooxidation of vinyl monomers will be more revealing.

An interesting question that emerges from the foregoing discussion is whether oxygen can permanently inhibit a radical polymerization reaction. In this laboratory, we have realized[115] that if the $RO_2^{\bullet}$ is diverted to yield a thermally stable product instead of the conventional polyperoxide, oxygen can permanently inhibit the polymerization. Furthermore, this approach would eliminate the temperature dependency of the inhibitory effect of oxygen in vinyl polymerization.

SCHEME IV. Important Steps in the Kinetics of PSP



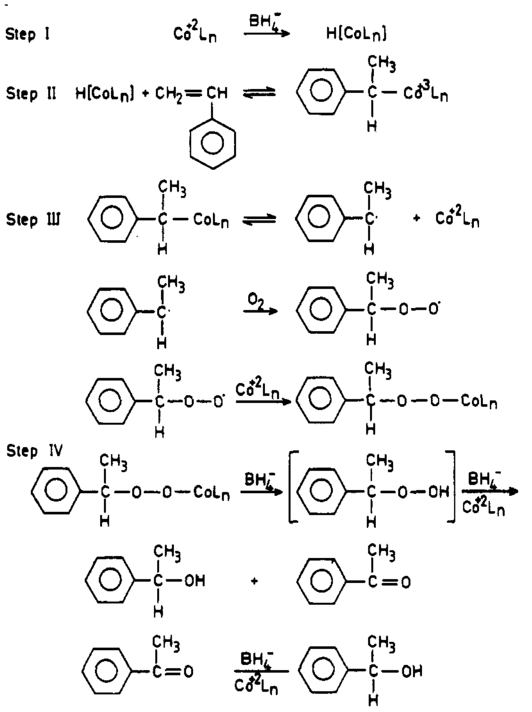
A suitable example of such a reaction was afforded[115] on the basis of a recent report by Okamoto and Oka[116] regarding the aerial oxidation of styrene like substrates. Okamoto and Oka[116] found that the Co^{2+}–BH_4^- redox system catalyzes the oxidation of various olefins to corresponding alcohols using aerial oxygen by a radical mechanism involving a peroxide intermediate (Scheme IV). They showed that a redox reaction is responsible for the generation of radicals from the olefinic substrate. The aerial oxygen then reacts with this radical to form a peroxide which subsequently yields the alcohol. In the specific case of styrene, we observed[115] that the $CH_3(C_6H_5)\dot{C}H$ radical intermediate (Scheme V) can initiate polymerization of excess styrene in the absence of oxygen. In the presence of aerial oxygen, the same radical yields 1-phenylethanol via a peroxide radical intermediate. The inhibitory action of oxygen can thus be attributed to the formation of 1-phenylethanol. And since the 1-phenylethanol is a thermally stable product, the inhibitory action of oxygen in the present case is permanent.

Many interesting facets of the polyperoxide chemistry have been reported in recent years. Cais and Bovey[114] studied the microstructure and molecular dynamics of poly(styrene peroxide) using ^{13}C NMR. Autopyrolyzability of poly(styrene peroxide) has been recently discovered by Kishore and Mukundan.[118] Amines are known[104] to decompose polyperoxides. This observation has been successfully exploited[119] to use poly(styrene peroxide) in combination with various amines as a redox initiator for room-temperature radical polymerization of vinyl monomers. Optically active poly(styrene peroxide) has been synthesized in the presence of optically active cobalt complex catalysts.[120]

B. Other Examples of Oxygen-Inhibited Polymerization Reactions

In the previous section we have discussed about the effect of intrusive oxygen on the kinetics of radical

SCHEME V. Mechanism of Okamoto–Oka Reaction



polymerization reactions. The retarding action of oxygen in such cases arises because of the facile formation of less reactive peroxidic radicals in preference to the usual propagating radicals. Apart from these mainly mechanistic studies, several miscellaneous reports are available in the literature regarding the manifestation of the inhibitory effect of oxygen under various reaction conditions, which are discussed below.

Sluggish reactivity of the peroxidic radicals during propagation step was considered to account for the inhibitory action of oxygen during polymerization of the oligo ester acrylates by Mogilevich et al.[121]

Louie et al.[122] explored the possibility of using the peroxide formation reaction in tackling the runaway problem in the batch production of emulsion polymerization of MMA. Though the above approach seems to be encouraging owing to a very high rate of the reaction of oxygen with the normal propagating radical, unfortunately an instantaneous termination also occurs in the presence of oxygen. This causes a substantial decrease in the molecular weight of the polymer, which, however, can be avoided by injecting very small quantities of oxygen in short "pulses". Thus, even the inhibitory action of oxygen can be beneficial if properly employed!

Lazaryants and Korchunov[123] reported the kinetics of polymerization of (diethylamino)ethyl methacrylate in the presence of oxygen. They observed that the polymerization rate constant had a normal value (8.5×10^{-5} L mol^{-1} s^{-1}), albeit a low efficiency of initiation. This was explained on the basis of monomer-induced accelerated decomposition of the polyperoxide which initiated the polymerization. Lavrov et al.[124] found that in the persulfate-ascorbic acid induced polymerization of 2-hydroxyethyl methacrylate, the atmospheric oxygen led to a decreased rate of polymerization. Also, the presence of oxygen caused increased reaction orders in the catalyst components, an increased activation energy and a reduction in the molecular weights of the resulting polymers.

Ozols and Parts[125] studied the kinetics of polymerization of acrylonitrile initiated by Fe^{3+}–H_2O_2 redox system at 26 °C in nitrogen atmosphere vitiated by different amounts of oxygen. Supplemental oxygen introduced into the system decreased the rate as well as the molecular weight of the resultant polymer. However, no difference in either the rate or molecular weight of the polymer was noticed when the amount of oxygen in nitrogen was reduced from 13.5 ppm to less than 1 ppm. An anomalous first-order dependence on irradiation intensity during radiation-induced polymerization of styrene, MMA, and acrylonitrile as well as the graft copolymerization onto natural rubber latex, was explained by Tsurugi et al.[126] on the basis of participation of oxygen in the termination step. The inhibitory effect of oxygen was found to decrease as the concentration of Fe^{2+} additive was increased during the acrylic acid homopolymerization.[127] The rate constant for the reaction of a peroxy radical with Fe^{2+} was found to be 400 times the propagation rate constant. During the preparation of hydroxy-terminated PMMA, oxygen was found to retard both the overall rate andd the conversion,[128] but molecular weight showed an increase. There are several other reports on the effect of oxygen on copolymerization[129–134] reactions, but they provide only qualitative information.

Acrylamide is one of the extensively studied examples of solid-state polymerization.[135–37] it is normally observed that if the polymerization takes place at the crystal surface, oxygen can retard the polymerization rate as well as reduce the degree of polymerization. On the other hand, if the propagation occurs well inside the crystal surface, oxygen cannot penetrate the surface and hence the polymerization proceeds without any interference by oxygen.

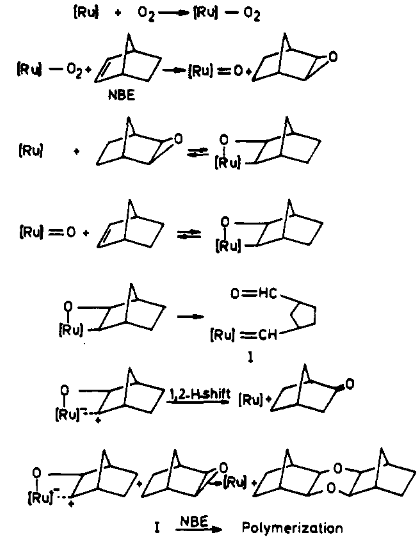
We have studied the melt polymerization of acrylamide by differential scanning calorimetry.[138,139] It was found from these studies that the thermal polymerization reaction follows radical mechanism,[138] and since oxygen can easily diffuse into the melt, a retarding effect of oxygen is observed in this polymerization. Quantitative studies[139] showed that the peak temperature of the polymerization exotherm shifts ahead by 8 °C in the presence of oxygen compared to the polymerization carried out in an inert atmosphere. Also, the overall heat released during the polymerization conducted in oxygen atmosphere is about 6 times less than the corresponding heat released in nitrogen atmosphere.

IV. Effect of Oxygen on Polymerization Catalysts

A. Metathesis Catalysts

Metathesis reaction of olefins is a useful method of preparing hydrocarbon polymers. The peculiarity of this method of polymerization involves the use of very different cocatalysts for the same metal complex catalysts, e.g., the typical Lewis acid $AlCl_3$ as well as the strong reducing agent *n*-butyllithium can be used with the catalyst WCl_6.[140] Banks and Kukues[141] reported a decline in the catalytic activity in the presence of oxygen for certain catalysts and an enhanced activity for others. Thoi et al.[142] have reported deactivation of the catalyst during polymerization of phenylacetylene. On the other hand, oxygen added in small quantities to

SCHEME VI. Role of Oxygen in Metathesis Polymerization



catalytic systems—both homogeneous[143-145] and heterogeneous[146]—is found to have a beneficial effect on catalyst activity. However, little is known about the exact chemistry of these reactions in the presence of oxygen. For example, in the case of $W(CO)_5(PPh_3)(I)$ catalyzed methathesis polymerization, oxygen was found to enhance the activity of the system I–$Al(Et)Cl_2$, but not that of I–$AlCl_3$. It was suggested[147] that oxygen reacts with $Al(Et)Cl_2$ to form a peroxide derivative. The peroxide being more acidic than $Al(Et)Cl_2$, facilitates the metal center to let off one of the carbonyl ligands in favor of the incoming monomer thus enhancing the polymerization.

In a particularly important paper, Ivin et al.,[148] during the $RuCl_2(PPh_3)_4$-catalyzed metathesis polymerization of norbornene (NBE), demonstrated that oxygen is probably involved in the formation of a key intermediate that subsequently initiates the polymerization; the rate of reaction was increased by as much as 100 times in the presence of oxygen! Based on the isolation and identification of a novel epoxide side product as well as a ketone, a plausible mechanism involving formation of oxometallacyclobutane and its subsequent rupture to form an initiating metallacarbene was proposed (Scheme VI). This scheme supposes that oxygen is incorporated into the polymer chain as a terminal carbonyl group; however, no evidence was reported for this hypothesis. Amass and McGourtey,[149] on the other hand, detected aldehydic end groups in the IR spectrum of a polymer obtained from metathesis polymerization of cyclopentene using WCl_6 as catalyst.

B. Ziegler–Natta Catalysts

Ziegler–Natta (Z–N) catalysts have a unique place in the synthesis of stereoregular polymers. Generally, their syntheses are carried out in an inert atmosphere to avoid the poisoning of the catalysts. However, it has also been shown[15] that additives such as water and oxygen among others have significant influence on the activity of the catalyst and hence on the polymer properties. The bimetallic catalysts are more drastically influenced by oxygen than the monometallic catalysts as far as tacticity changes are concerned. This is corroborated in the following discussion.

Masuda and Takami,[150] on the basis of earlier reports[151,152] on the sensitivity of Z–N catalysts to oxygen, studied the system $Et_2AlCl–TiCl_3$ in detail. They found that the different polymerization effects are observed if the sequence of mixing of the metallic components is changed for two experiments conducted in the presence of oxygen. In the first case, $TiCl_3$ was added to an Et_2AlCl-containing solution exposed to oxygen and in the second, Et_2AlCl was added to a heptane solution of $TiCl_3$ exposed to oxygen. It was found that the catalyst prepared by the first method showed a marked improvement in catalytic activity without a decrease in the stereoregularity of the polymer up to an O_2–Al ratio of 0.6. The activity decreases significantly at higher O_2–Al ratio (>1.2), owing to the formation of an EtAl(OEt)Cl type of the oxidation product which is usually obtained from the oxidation of Et_2AlCl. In the second case, a lower activity was observed, which may be due to the formation of catalytically inactive Ti species.

Dubinkova et al.[153] published the first report on the effect of oxygen on the supported Ziegler type catalyst. They studied the system, VCl_4/perlite–Al(*i*-Bu)$_3$. Here also, two different experiments were performed to determine the reaction product of oxygen with each metal center and the resulting consequence on the catalyst activity. When the vanadium compound was added after exposing the aluminum component to oxygen, the catalytic activity decreased at an O_2–Al ratio of about 0.2. It was found that Al(*i*-Bu)$_3$ was oxidized to (*i*-Bu)$_2$Al(*i*-BuO) which was proved to be responsible for the reduced activity in a separate experiment carried out in the liquid phase (using hexane as a solvent). In the other experiment, when the vanadium component was first exposed to oxygen, the catalytic activity was enhanced. This was attributed to the oxidation of vanadium to a higher valent state, for example $VOCl_3$, which exhibits increased activity in olefin polymerization.[153] When oxygen interacted with the catalyst obtained after mixing of the two components, complete inhibition was observed.

Boor and Youngman[154] studied the effect of oxygen on the preparation of syndiotactic polypropylene employing the Z–N catalyst, Al(*i*-Bu)$_3$–VCl_4. The effect of additives on the syndiotacticity was compared on the basis of the index ratio $A_{11.53}/0.5(A_{2.32} + A_{2.35})$ where $A_{11.35}$ represents the absorbance at the 11.53 μm band in the IR spectrum of the polymer, $A_{2.32}$ and $A_{2.35}$ being the absorbance values at the subscripted wavelengths. A higher value of the index ratio implies a higher syndiotacticity. For the polymer obtained in the absence of oxygen, the index ratio was 1.2. With the additions of 40 and 75 mL of oxygen to VCl_4 followed by mixing with Al(*i*-Bu)$_3$ yielded polymers with the index ratios of 1.4 and 1.8, respectively. Furthermore, the sequence of additions of oxygen and the catalyst components were reported to be important. Mixing of 100 mL of oxygen and Al(*i*-Bu)$_3$ prior to the addition of VCl_4 yielded syndiotacticity index of 1.8 only.

It can thus be safely concluded that the effect of oxygen on Z–N catalysts, bimetallic in particular, depends upon which of the bimetallic components is exposed to oxygen prior to mixing with the other component. Further, this effect may be entirely different from the effect of oxygen on the "preformed" catalyst.

The topic, though interesting, has not received sufficient attention in spite of the fact that hundreds of combinations of bimetallic Z–N catalysts have been known for quite some time. It appears that involvement of oxygen in the Z–N polymerization is promising for developing cheaper methods of synthesizing tailor-made stereoregular polymers.

C. Miscellaneous Reports

Report by Matsumoto et al.[155] that oxygen, peroxides, and iodine introduce stereospecificity in crotylnickel halides initiated butadiene polymerization was disproved by Wallace and Harrod.[156] Although the exact reaction in the presence of oxygen was not known, it was suspected that oxygen reacts with the nickel complex to form an inactive species. This reaction was found to be very slow and the catalyst pretreated with oxygen, surprisingly, gave a high molecular weight polymer. The microstructure of this polymer was not different from that obtained by using an unpoisoned catalyst. On the other hand, in the case where additives were introduced during polymerization, a slight increase in the cis content of the resulting polymer was found. This was explained by assuming that the above deactivation reaction proceeds through the formation of some unidentified radicals, which promote the formation of *cis*-polybutadiene.

The transition metal chelates are well-known initiators of free-radical vinyl polymerization. Oxygen has been reported[157] to inhibit the polymerization initiated by such complexes. A very interesting phenomenon of catalytic chain transfer using a cobalt(II) porphyrin complex was reported by Yenikolopyan et al.[158] The distinction of this agent from a conventional chain transfer agent lies in its characteristic ability to bring about the transfer reaction hundreds of times, thus reducing the molecular weight significantly. Pliss et al.[159] reported that the peroxy radical generated in the presence of oxygen reacts with the above complex to form Co(III) and hampers the catalytic chain transfer. The cation radical induced polymerization of olefins by the catalyst $EtAlCl_2$ was found to be inhibited by oxygen.[160] The free-radical polymerization of MMA catalyzed by silica and metal oxides like alumina was also reported to be inhibited by oxygen.[161] Finally, Ryabova[162] suggested that the emulsion polymerization of styrene catalyzed by $K_2S_2O_8$ suffered a long induction period since oxygen inhibited the decomposition of the catalyst.

V. Influence of Oxygen on the Properties of Polymers

Oxygen can either improve or deteriorate various polymer properties. Changes in the chain configuration because of the chemical changes introduced by reaction of oxygen with Z–N catalysts have been discussed earlier. Poly(vinylidene fluoride) prepared by conventional radical polymerization initiators contains about 10% imperfections.[163] Trialkylborane–oxygen catalyst was found[164] to yield a polymer with only 3% head-to-head and 3% tail-to-tail imperfections as against the 2.7% imperfection content obtained with the conventional Z–N catalyst. Orshikin et al.[165] found that the π-crotyl complexes of chromium catalyze the polymerization of butadiene to a predominantly 1,2-polybutadiene with small amounts of *trans*-1,4-polybutadiene. On the other hand, in the presence of added oxygen, the main product was of the latter type. When more and more crotyl groups were substituted by chlorine in the parent chromium complex, the percentage of *cis*-1,4-polybutadiene was found to increase. This result needs to be verified in the light of results obtained by Wallace and Harrod.[156]

Oxygen-initiated ethylene polymerization yields a polymer having properties like density, short chain branching etc., not much different from the polymer obtained under nitrogen atmosphere.[166] In fact some patents report that improved polymer properties, like high melt index,[167] better optical properties,[168] good stress-cracking resistance,[169] high drawability, and adhesion,[170] were obtained only in case of processes involving the presence of oxygen. However, a disadvantage of polyethylene prepared under oxygen atmosphere was that the long chain branching was higher than for the polymer obtained under nitrogen atmosphere and consequently, the molecular weight distribution (MWD) was broader for the polymer prepared in oxygen.[171]

An extreme case of broadening of MWD of polymer prepared in the presence of oxygen has been reported[172] for bulk photopolymerization of MMA induced by acetophenone-based initiator. The dead polymer molecule bearing the terminal benzoyl peroxide type end group was postulated to undergo a photocleavage, bringing about the formation of additional high molecular weight species, and hence a bimodal MWD curve. Broadening of MWD in MMA polymerization was also found to result because of the presence of peroxide macroradicals generated in the presence of oxygen.[173] On the other hand, McGinnis et al.[174] during the bulk photopolymerization of MMA observed that the polymer prepared under oxygen atmosphere possesses a narrower distribution than the one prepared in nitrogen. On the basis of the experiments carried out in inert atmosphere, they found that polydispersity index was less than 2, indicating that usual biradical termination is absent and primary radical termination or chain transfer or photoinitiator radical or photoproduct is predominant. In the presence of oxygen, a faster additional reaction competes with the photochemically generated radicals or the photoproducts:

$$R^{\bullet} \rightarrow RO_2^{\bullet} \text{ or } R^{\bullet} + RO^{\bullet} \rightarrow \text{inactive products}$$

This was considered to be the reason for comparatively narrower MWD observed in the presence of oxygen.

PVC is one of the most widely used thermoplastics. However, the commercially manufactured material is very often found to be thermally and photochemically unstable. It was suspected for a long time that oxygen containing groups get incorporated in the PVC backbone to render it unstable. The detailed studies reported from various groups confirm that instability of PVC arises because of carbonyl containing structures.[175] On the basis of this background, Braun et al.[176] carried out polymerization of vinyl chloride in presence of deliberately added small quantities of oxygen. Their results show that vinyl chloride is a very interesting monomer in that the alternate peroxide copolymer which it forms with oxygen starts degrading soon after its formation, and CO was found to be the main degradation product. Braun et al.[176] further suggested that this liberated CO neither escapes the system nor adds straightaway to vinyl chloride to form an inchain copolymer. Instead, the radical formed after the addition of CO to vinyl chloride radical end undergoes rearrangement to introduce chlorocarbonyl pendant groups as suggested by Ratti et al.[177]

Wescott et al.[178] have recently confirmed the structure in eq 66 of the vinyl chloride–carbon monoxide copolymer on basis of the NMR studies of the appropriate model compounds. They also concluded that, when

$$-CH_2-\dot{C}HCl + CO \rightarrow -CH_2CHCl-CO^{\bullet} \xrightarrow{\text{rearrangement}} -CH_2-\dot{C}H-COCl \xrightarrow{\text{vinyl chloride}} -CH_2-CH(COCl)-CH_2-\dot{C}HCl- \quad (66)$$

copolymerization of vinyl chloride is carried out with CO at 50 °C and above CO pressure of 6.5 atm, mechanism of Ratti et al.[177] holds good for the free-radical copolymerization of vinyl chloride and CO.

Conducting polymers have assumed a lot of significance in last few years because of their possible applications in power transmission and other areas. Polyacetylene is the single most thoroughly studied polymer of this class. This and most of the film-forming conducting polymers suffer from the disadvantage of inherent air instability. In fact the detailed studies[179] on polyacetylene have proved that initial "doping" reaction responsible for the initial increased conductivity is soon overtaken by degradation, which leads to the formation of carbonyl and hydroperoxide groups and a decrease in conductivity.

VI. Summary and Outlook

It is clear from the foregoing discussion that oxygen appears to exhibit two contrasting roles in polymerization reactions, both as an initiator and as an inhibitor. Interestingly, in the unique case of high-pressure ethylene polymerization it plays both the roles.

Quite naturally, role of oxygen in the initiation has been studied more extensively. However, a deeper understanding of these processes is lacking, particularly because of the formation of labile intermediates in the presence of oxygen. Nevertheless, the progress achieved so far has certainly added to our present knowledge of the oxidation and autooxidation reactions of various polymerizable substrates. It is also apparent that some of the reactions of oxygen can be favorably exploited. Noteworthy among these are (i) use of oxygen as a cheap initiator and/or a cocatalyst to increase the rate or yield of polymerization, (ii) control of the stereoregularity in Z–N polymerization, (iii) prevention of the "runaway" problem in industrial polymerization processes, and (iv) the synthesis of useful block copolymers.

The negative manifestations of oxygen on the polymerization processes include interpolation of an induction period, reduction in the rate of polymerization or in extreme cases, complete inhibition, catalyst poisoning, etc. Unfortunately, our perception of the reactions responsible for these detrimental effects is not satisfactory at present. It is imperative that deeper studies in this direction are required not only for the clearer understanding of the inhibitory action of oxygen, but also to explore the pathways to beneficially utilize oxygen in polymerization reactions.

Judging the overall information available so far on the role of oxygen in polymer chemistry, we believe that some attractive topics worth pursuing appear to be (a) isolation and characterization of the catalysts for phenolic coupling reactions, (b) detailed study of the kinetics of autooxidation of trialkylboranes and the kinetics of corresponding polymerization reactions, (c) fundamental studies for unravelling the chemistry behind the beneficial effects of oxygen on various polymer properties like molecular weight and MWD, (d) analysis of the oxidation products of metathesis, Friedel–Crafts, and Ziegler–Natta type catalysts (desirable from point of view of organometallic chemistry as well), and, finally, (e) specific studies on the effects of these oxidized species on the course of polymerization and the resultant polymer properties.

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