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Heinz Grünig^a; Pe-Chin Lim^a; Gerhard Luft^a; Hans Seidl^b

^a Institut für Chemische Technologie, Darmstadt, West Germany ^b Peroxid-Chemie GmbH, Höllriegelskreuth, Munich, West Germany

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The Effect of Oxygen on Conversion in the Organic Peroxide-Initiated High-Pressure Polymerization of Ethylene

HEINZ GRÜNIG, PE-CHIN LIM, and GERHARD LUFT

Institut für Chemische Technologie
6100 Darmstadt, West Germany

HANS SEIDL

Peroxid-Chemie GmbH
Höllriegelskreuth (Munich), West Germany

ABSTRACT

To initiate the high-pressure polymerization of ethylene, oxygen is used together with organic peroxides in a number of tubular reactor processes. Since molecular oxygen is capable of promoting or inhibiting radical polymerization, depending on the reaction conditions chosen, controlled experiments were carried out to clarify these aspects of high pressure ethylene polymerization. In continuous polymerization tests carried out at 1700 bar and temperatures between 110 and 320°C, conversions were determined with tert-amyl perneodecanoate and di-tert-butyl peroxide initiation in the presence of various quantities of oxygen. Batch tests using a photo-initiator together with oxygen were also carried out. A comparison with polymerizations under conditions of careful elimination of oxygen shows no effect on the peroxide-initiated polymerization up to temperatures of 160 to 170°C. Although oxygen is an initiator at higher temperatures,

the conversions obtained from the simultaneous addition of controlled quantities of oxygen and organic peroxides is lower than that obtained by adding together the conversions from the separate polymerizations.

INTRODUCTION

Molecular oxygen is used as an initiator in the high-pressure synthesis of polyethylene according to the tubular reactor process. It has the advantage of being cheap and easy to handle [1, 2]. However, the use of oxygen is limited to relatively high temperature ranges since it is only capable of initiating high-pressure polymerization above 160 to 170°C. This limits the conversion potential and prevents the efficiency of the tubular reactor from being fully exploited.

To increase the profitability of polyethylene synthesis, organic peroxides can additionally be metered into the reactor to initiate polymerization at lower temperatures of 120-130°C [3-5]. A small additional investment will thus increase conversion by 10 to 30%.

This provides no answer to the question of whether oxygen has an inhibiting effect upon peroxide-initiated polymerization, resulting in an increased peroxide requirement. On the other hand, it is conceivable that the initiation mechanisms take place independently, and the possibility of the polymerization process being accelerated by a synergetic effect cannot be discounted.

INVESTIGATION OF THE POLYMERIZATION-INHIBITING EFFECT OF OXYGEN

A fundamental investigation into the polymerization inhibition by molecular oxygen was published by Schulz [6] in 1955. He was able to prove that the polymerization of methyl methacrylate initiated by azoisobutyronitrile (AIBN) at 50°C and normal pressure is temporarily delayed in the presence of oxygen. According to Schulz, the period of inhibition τ_r is proportional to the oxygen concentration (O_2) and decreases with an increasing monomer (M) and initiator concentration (I):

$$\tau_r = A(I)^{-1/2}(M)^{-1}(O_2) \quad (1)$$

During the inhibition period, a strictly alternating copolymerization takes place between molecular oxygen and monomer. The alternation is due to the fact that the addition of oxygen to a radical chain

end takes place at a rate which exceeds the rate of monomer addition by at least 5 orders of magnitude. The reactivity of oxygen in this reaction corresponds to that of a free radical.

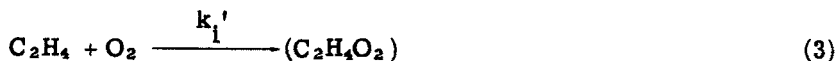
Similar results were obtained by Henrici-Olivé and Olivé [7] who examined the system styrene/AIBN/oxygen at 50°C and normal pressure.

During the oxygen-initiated polymerization of ethylene, Ehrlich [8] was able to observe an induction period which is greatly influenced by the pressure and the temperature, but only slightly by the oxygen concentration. Ehrlich established the following function for a temperature of 130°C:

$$\tau_i = Ap^{-1}(O_2)^{0.2} \quad (2)$$

He also considers it probable that peroxides are formed either by the addition of ethylene to oxygen or by copolymerization. In his opinion, the chain start is initiated by the thermal decomposition of these polyperoxides [9].

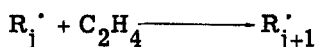
An induction period was also discovered by Gierth [10] during the polymerization of ethylene at temperatures up to 170°C and pressures of up to 2200 bar. He assumes that the polymerization is initiated by the formation of an interaction product of ethylene and oxygen but provides no information on its composition.



Under the influence of thermal energy, radicals are formed from the interaction product,



which are added on to the monomer:



Since the interaction product ($C_2H_4O_2$) cannot be detected, its decomposition according to Eq. (4) is likely to take place very rapidly, i.e., $k_i'' \gg k_i'$. The radical R_1' obtained from the interaction product and the polymer radical R_j' are scavenged by the excess oxygen and converted into an inactive species R:



The length of the inhibition period is determined by the effect of the competing Reactions (3) to (6). The polymerization reaction begins only when a sufficient number of radicals have been formed and the concentration of free oxygen has been reduced to a level such that it is incapable of immediately blocking every newly formed radical.

Tatsukami [11] uses a similar concept; in his equation representing the rate of ethylene polymerization, the inhibiting effect of oxygen is expressed by a term which combines the inhibition reaction rate constant k_r and the oxygen and ethylene concentration:

$$r_{Br} = k_w (k_s/k_a)^{1/2} (C_2H_4)(O_2)^{1/2} - k_r (k_w/2k_a)(C_2H_4)(O_2) \quad (7)$$

Steiner and Schoenemann [12] carried out investigations into the high-pressure ethylene polymerization with AIBN in the presence of comparable quantities of atmospheric oxygen. In this batch-type process, the polymerization reaction is initiated at low temperatures by the readily decomposing AIBN. The heat evolved in the reaction causes the temperature to rise, and at 160-170°C and above, a second polymerization reaction is initiated by the oxygen added.

EXPERIMENTS

To investigate the influence of oxygen on organic peroxide-initiated polymerization processes, experiments were carried out in a continuously operating stirred autoclave. The same equipment and technique were used as for previous investigations [13]. In order to cover a wide temperature range, an active peroxide, namely tert-amyl perneodecanoate, and a more stable peroxide, namely di-tert-butyl peroxide, were used. The temperature giving a half-life of 1 min ($T_{1/2}$) is 124°C for tert-amyl perneodecanoate (Table 1). This peroxide is capable of initiating ethylene polymerization at temperatures below the so-called "initiation temperature" of oxygen of 160-170°C. Di-tert-butyl peroxide decomposes into radicals at higher temperatures ($T_{1/2} = 190^\circ\text{C}$) and was therefore chosen for the polymerization experiments at temperatures greater than 170°C.

The peroxides were dissolved in iso-dodecane to a concentration of 10 mol ppm and the solutions were mixed with the ethylene passing into the reactor. At the same time, 6-90 mol ppm oxygen was also metered into the reactor (Table 2). For purposes of comparison, polymerization reactions were carried out with 10 and 40 mol ppm

TABLE 1. Peroxides

Peroxide	Formula	Molecular weight	Temperature for a half-life of 1 min (°C)
tert-Amyl perneo-decanoate	$ \begin{array}{c} \text{CH}_3 \quad \quad \text{O} \quad \text{R}_1 \\ \quad \quad \quad \quad \\ \text{C}_2\text{H}_5-\text{C}-\text{O}-\text{O}-\text{C}-\text{C}-\text{CH}_3^a \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{R}_2 \end{array} $	260.4	124
Di-tert-butyl peroxide	$ \begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3-\text{C}-\text{O}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array} $	146.2	191

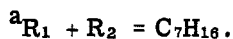


TABLE 2. Experiments in the Continuously Operating Autoclave (pressure 1700 bar, residence time 40 s)

Peroxide	Peroxide concentration (mol ppm)	Oxygen concentration (mol ppm)	Temperature (°C)
tert-Amyl perneo-decanoate	10	-	104-235
	40	-	
Di-tert-butyl peroxide	10	-	237-293
	40	-	
-	-	2	190-320
	-	10	
	-	30	
	-	50	
	-	80	
tert-Amyl perneo-decanoate	10	50	110-286
	10	90	

(continued)

TABLE 2 (continued)

Peroxide	Peroxide concentration (mol ppm)	Oxygen concentration (mol ppm)	Temperature (°C)
Di-tert-butyl peroxide	10	6	236-284
	10	18	
	10	37	
	10	60	

peroxide, respectively, without the addition of oxygen, and with oxygen alone in concentrations of 2 to 80 mol ppm. In all cases a pressure of 1700 bar was used and the residence time was 40 s.

After leaving the reactor, the polymer formed under conditions giving a constant pressure, temperature, and initiator level was separated from the unreacted ethylene by reducing the pressure to normal levels. The amount of polymer obtained per unit of time and the flow rate of ethylene into the reactor were used to determine the conversion; the amount of polymer obtained and the amount of peroxide introduced into the process were used to calculate the peroxide consumption.

The graph at the top of Fig. 1 shows the conversion obtained in the polymerization initiated with tert-amyl perneodecanoate as a function of the temperature. The course of the curves is typical of the peroxide-initiated polymerization of ethylene. The conversion/temperature curves exhibit a steep initial rise with increasing polymerization temperatures, and level off subsequently.

The addition of 50 or 90 mol ppm oxygen does not alter the conversion curve within the low temperature range (bottom graph, Fig. 1). Up to a temperature of 160-170°C, the course of the curve is identical with the curve representing the polymerization initiated with 10 mol ppm tert-amyl perneodecanoate alone. However, with polymerization temperatures $T > 170^\circ\text{C}$, the conversion curves begin to rise again.

In the case of di-tert-butyl peroxide, the slope of the conversion curves rises more steeply initially, with increasing temperatures, and levels off subsequently (Fig. 2, broken lines). The conversion is higher than in the case of tert. amyl perneodecanoate initiation at identical polymerization temperatures. With an addition of oxygen, a higher conversion is obtained than from the polymerization initiated with peroxide alone (Fig. 2, continuous lines).

In the case of polymerizations carried out with oxygen alone, the conversion obtained within the range investigated increases with the polymerization temperature (Fig. 3, left-hand side). The correlation between the conversion and the oxygen concentration follows the well-known mathematical law of roots.

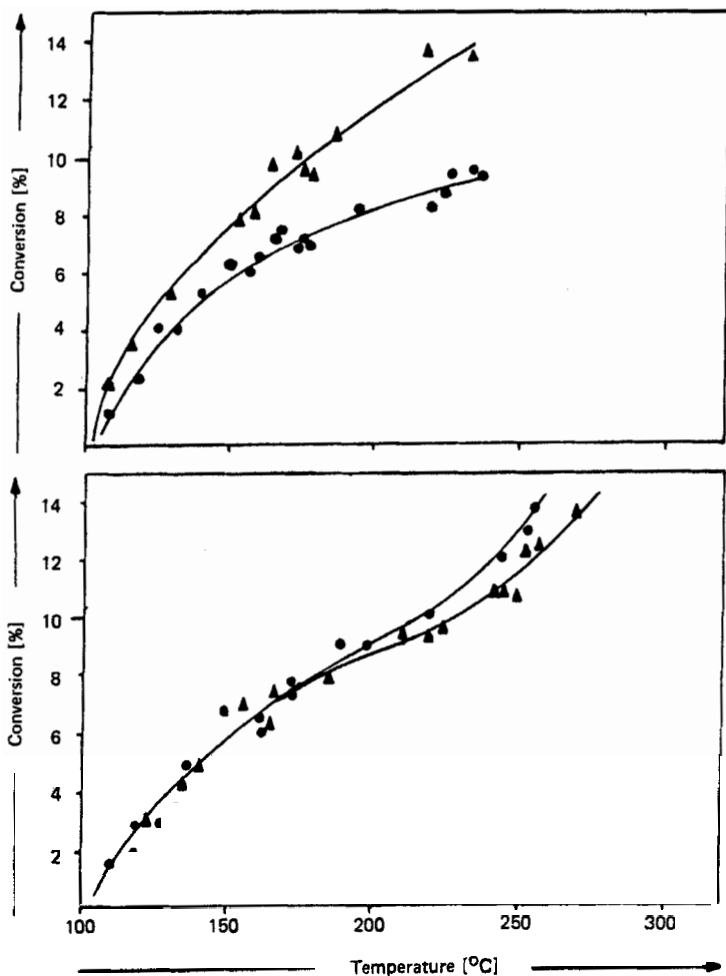


FIG. 1. Polymerization with *t*-amyl perneodecanoate. Pressure: 1700 bar. Residence time: 40 s. Top: (▲) 40 mol ppm *tert*-amyl perneodecanoate, (●) 10 mol ppm *tert*-amyl perneodecanoate. Bottom: (▲) 10 mol ppm *tert*-amyl perneodecanoate and 50 mol ppm oxygen, (●) 10 mol ppm *tert*-amyl perneodecanoate and 90 mol ppm oxygen.

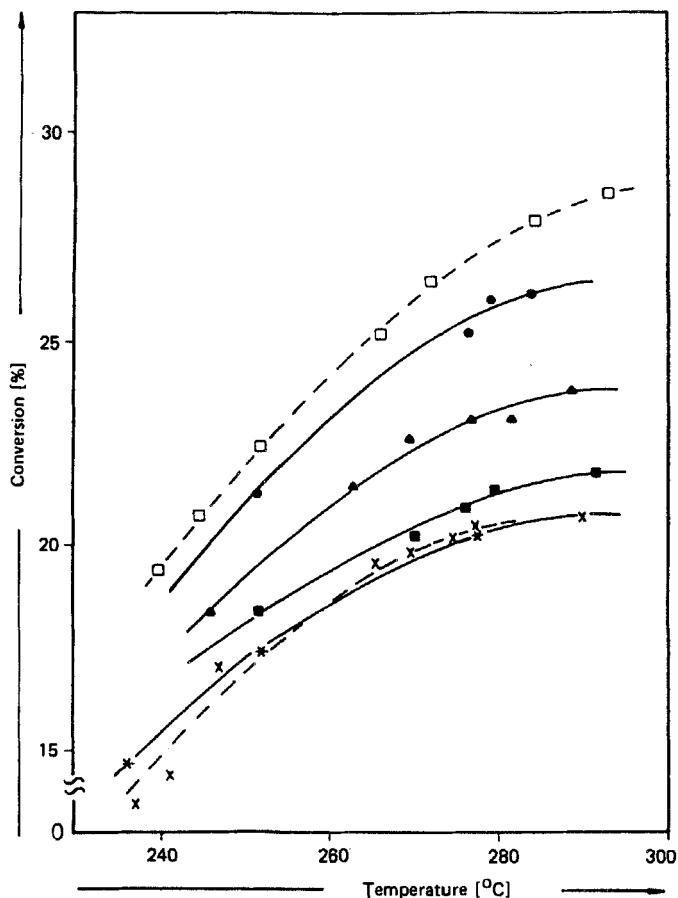


FIG. 2. Polymerization with di-tert-butyl peroxide. Pressure: 1700 bar. Residence time 40 s. Broken lines: (x) 10 mol ppm di-tert-butyl peroxide, (□) 40 mol ppm di-tert-butyl peroxide. Continuous lines: 10 mol ppm di-tert-butyl peroxide and (*) 6 mol ppm oxygen, (■) 18 mol ppm oxygen, (▲) 37 mol ppm oxygen, (●) 60 mol ppm oxygen.

Most of the work on the effect of oxygen published so far involves batchwise polymerization techniques. In addition to the continuous polymerization tests, batchwise tests were carried out at temperatures below the "initiation temperature" of oxygen. Batchwise polymerization presents the problem of radicals being actually formed during the addition of reactive peroxides to the monomer.

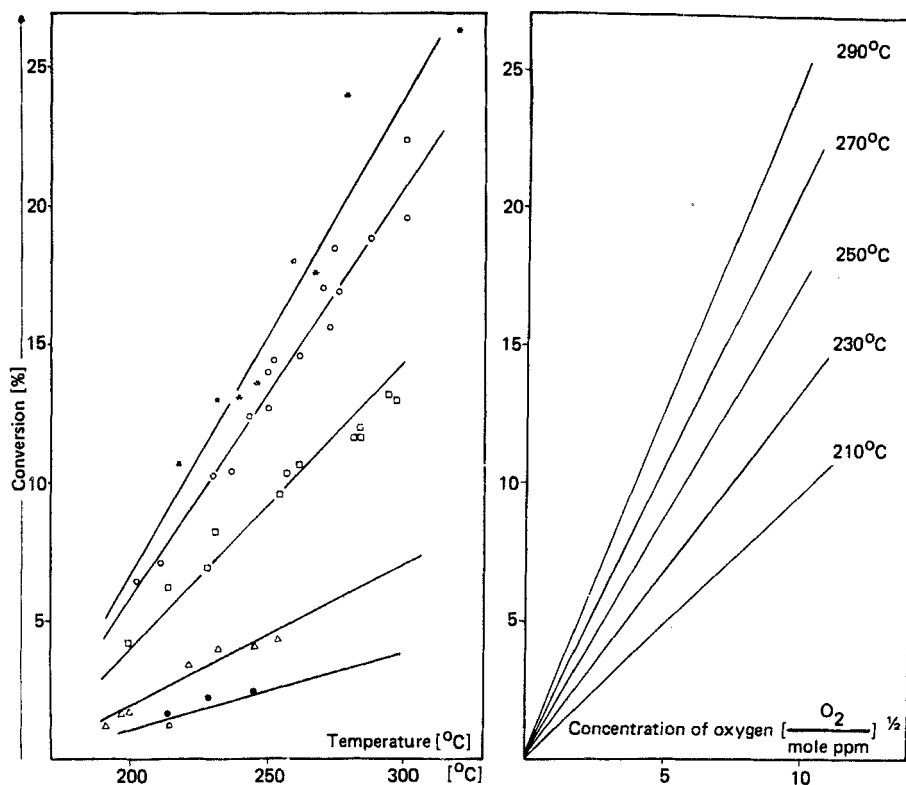


FIG. 3. Polymerization with oxygen. Pressure: 1700 bar. Residence time 40 s.

Curve	Oxygen (mol ppm)
●	2
△	10
□	30
○	50
*	80

For this reason, a photo-initiator, namely diphenyl disulfide, was used. Preliminary experiments had shown that this initiator undergoes practically no thermal decomposition at temperatures below 150°C. The experiments were carried out in a 100-mL stirred autoclave equipped with a sapphire window. The focused beam of light of a mercury high-pressure vapor lamp was filtered to obtain a ray with a wavelength of 360 μm . Light of this wavelength has an excitation effect on the photo-initiator but is not absorbed by ethylene.

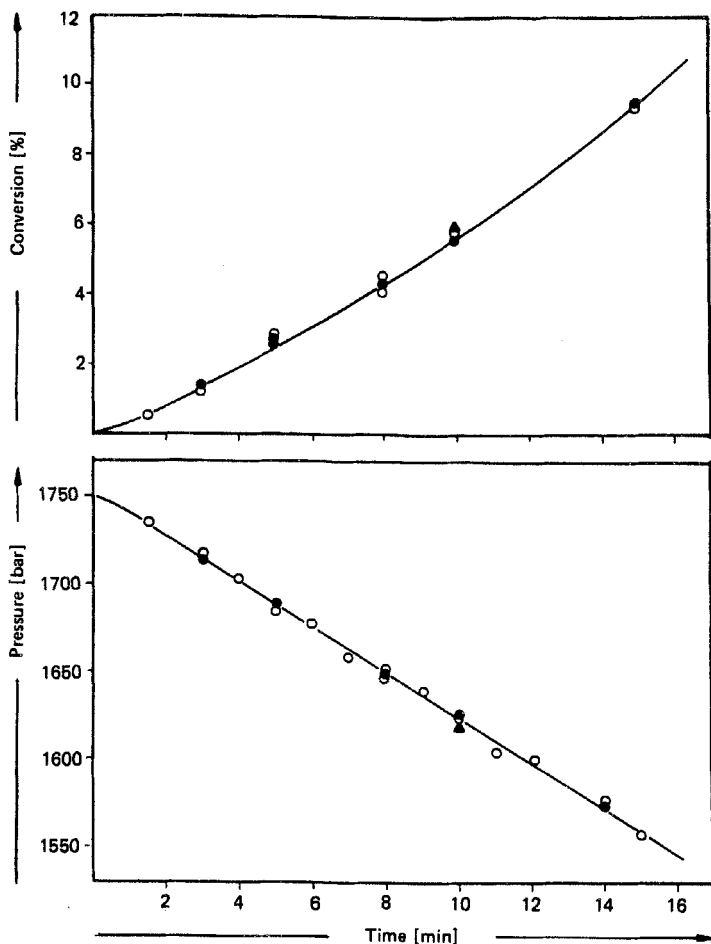


FIG. 4. Batchwise polymerization in the presence and in the absence of oxygen. Pressure: 1550 to 1750 bar. Temperature: 150°C. Top: Conversion as a function of time. Bottom: Decrease of pressure.

	Diphenyl disulfide (mol/mL)	Oxygen (mol/mL)
○	2.75×10^{-6}	-
●	2.75×10^{-6}	9.2×10^{-7}
▲	2.75×10^{-6}	4.6×10^{-6}

In preparation for a polymerization test, the stirred autoclave was evacuated and heated to the test temperature. The photo-initiator, dissolved in *n*-heptane, was then introduced and ethylene was supplied under pressure through a diaphragm compressor. The reactants were mixed with a high-speed magnetic stirrer. Polymerization was then initiated by opening a diaphragm blocking the ray of light.

In each experiment the conversion obtained with a certain light intensity and an initial initiator concentration of 2.75×10^{-6} mol/mL was measured as a function of time. The initial pressure was 1750 bar. It decreased by a maximum of 200 bar as a result of the monomer reaction. In one series of polymerization tests, great care was taken to eliminate the presence of oxygen. In another series of experiments, 9.2×10^{-7} mol/mL (50 mol ppm) oxygen were added. To obtain a conversion/time curve, the polymerization tests were stopped after predetermined periods of time by relieving the reactor pressure and the quantity of polymer formed was then determined by gravimetry.

The conversion/time curves thus determined are plotted in the top graph of Fig. 4. The experiments under exclusion of oxygen are represented by circles and the experiments with addition of oxygen by dots. Within the accuracy of measurement the conversion/time curves are the same in the presence and in the absence of oxygen. No differences are found even with very high oxygen concentrations of 4.6×10^{-6} mol/mL (250 mol ppm). This also applies of course to the pressure/time curves where a polymerization inhibition would be clearly illustrated by a delay and reduced pressure loss.

Their slope is first gradual, then exponential, and finally approaches a maximum conversion value when the photo-initiator has been consumed.

DISCUSSION OF THE CONVERSION MEASUREMENTS

Two temperature ranges must be distinguished in a discussion of the experimental results. To initiate high-pressure ethylene polymerization with oxygen, temperatures of at least 160-170°C are required. This is a well-known fact and is illustrated by the graph on the left-hand side of Fig. 3. When the curves thus obtained are extrapolated to zero conversion, they intersect at this temperature. At temperatures below this so-called initiation temperature, oxygen acts neither as an initiator nor as an inhibitor of a peroxide-initiated ethylene polymerization. This has been shown by the results of both the continuous and the batchwise experiments. An addition of 50 or 90 mol ppm oxygen has no effect on a *tert*-amyl perneodecanoate-initiated polymerization in the continuously operating stirred autoclave if the polymerization temperature is below 160-170°C (Fig. 1, bottom graph).

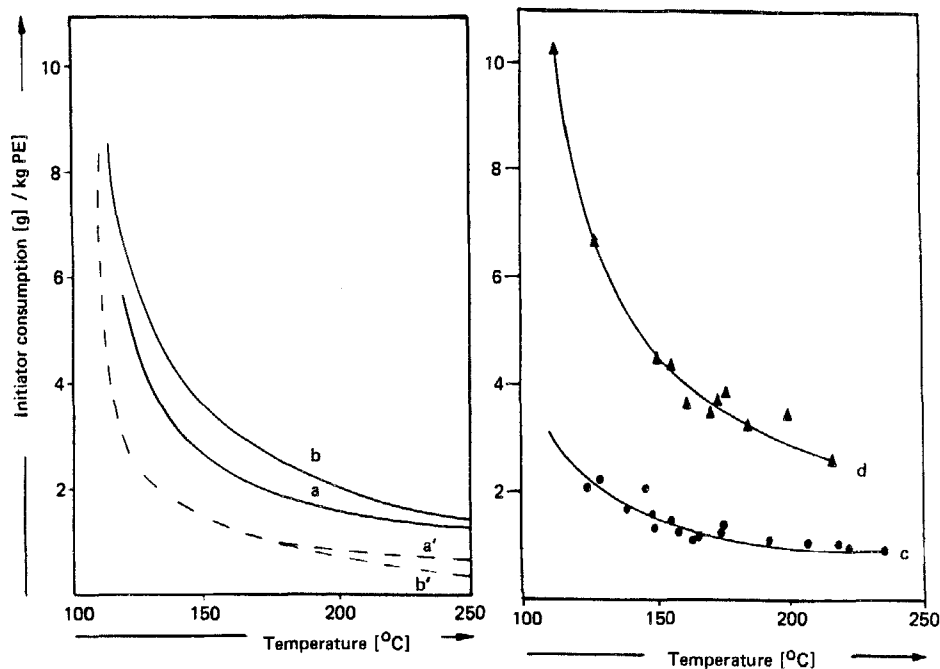


FIG. 5. Peroxide consumption in the polymerization with tert-amyl perneodecanoate at low and elevated temperatures. Pressure: 1700 bar. Residence time: 40 s. Left: Peroxide consumption in the presence of oxygen. Right: Peroxide consumption in the absence of oxygen.

Curve	Peroxide (mol ppm)	Oxygen (mol ppm)
a, a'	10	50
b, b'	10	90
c	10	-
d	40	-

The presence of oxygen during a batchwise photo-initiated polymerization affects neither the conversion nor the time scale of the conversion or the pressure curves (Fig. 4).

However, the conversion is increased by the addition of oxygen if the polymerization process is carried out at temperatures above the initiation temperature of oxygen. The conversion increases with increasing oxygen concentrations both in polymerizations initiated with tert-amyl perpivalate (Fig. 1, bottom graph) and di-tert-butyl

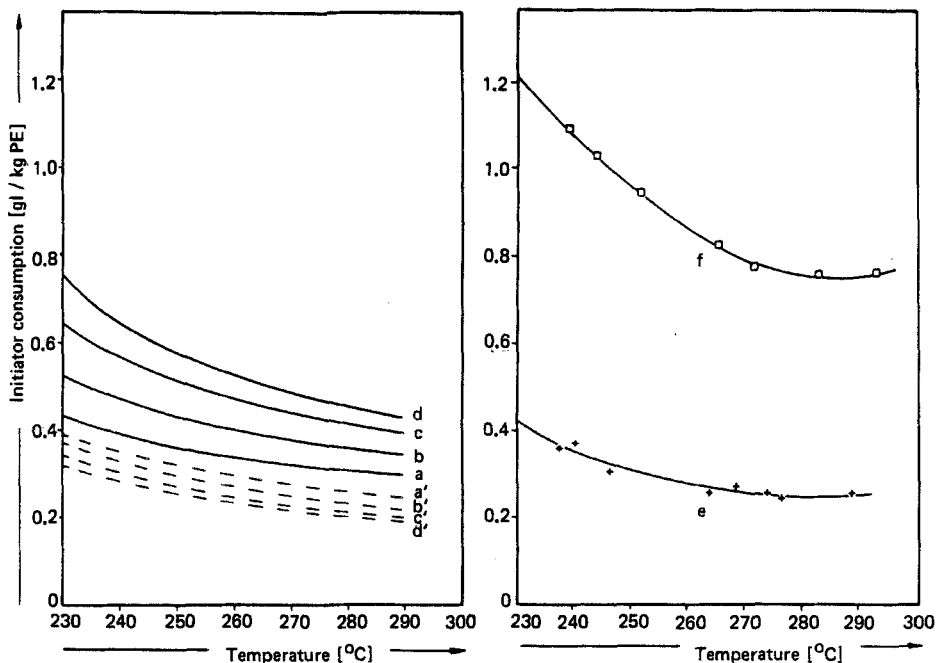


FIG. 6. Consumption of di-tert-butyl peroxide and oxygen at elevated temperatures. Pressure: 1700 bar. Residence time: 40 s. Left: Polymerization in the presence of oxygen. Right: Polymerization in the absence of oxygen.

Curve	Di-tert-butyl peroxide (mol ppm)	Oxygen (mol ppm)
a, a'	10	6
b, b'	10	18
c, c'	10	37
d, d'	10	60
e	10	-
f	40	-

peroxide (Fig. 2). In this temperature range, oxygen contributes toward the initiation of the high-pressure ethylene polymerization.

The initiator consumption provides a further illustration of the effect of oxygen in the two temperature range. It is plotted in Fig. 5

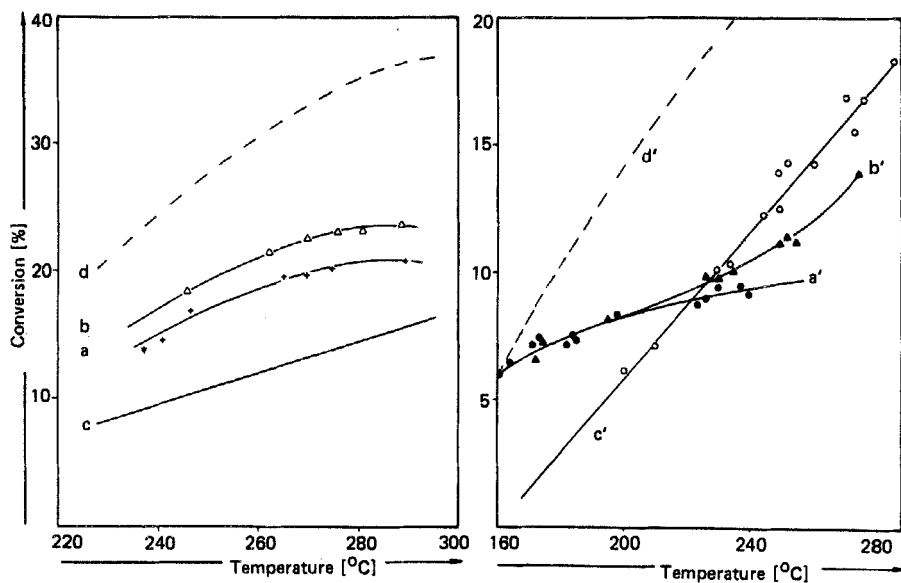


FIG. 7. Conversion in the presence of oxygen compared with the conversion obtained in separate experiments with peroxide or oxygen. Left: Di-tert-butyl peroxide.

Curve	Di-tert-butyl peroxide	Oxygen
a	10	-
b	10	37
c	-	37
d	10	-
	-	37

Right: tert-Amyl perneodecanoate.

Curve	tert-Amyl perneodecanoate	Oxygen
a'	10	-
b'	10	50
c'	-	50
d'	10	-
	-	50

as a function of the polymerization temperature. The broken lines in the graph on the left-hand side of Fig. 5 represent the consumption of tert-amyl perneodecanoate per kg polyethylene formed. It is a well-known fact that it decreases with increasing polymerization temperatures. At temperatures $T < 160^{\circ}\text{C}$, the consumption curves obtained from the series of tests using additions of 50 and 90 mol ppm oxygen are identical and coincide with the consumption curves obtained by adding peroxide alone (Fig. 5, right-hand side, Curve c). At $T > 160^{\circ}\text{C}$, the consumption curves in Fig. 5, left-hand side, split into two. The consumption based on tert-amyl perneodecanoate decreases with increasing additions of oxygen since oxygen is a co-initiator in the polymerization reaction. The combined consumption of peroxide and oxygen is represented by the continuous curves in Fig. 5, left-hand side. It should be noted that oxygen does not contribute toward the polymerization initiation at low temperatures ($T < 160^{\circ}\text{C}$).

The simultaneous initiation of polymerization at elevated temperatures is also illustrated by the consumption curves obtained from the experiments with di-tert-butyl peroxide in the presence of different amounts of oxygen (Fig. 6, left-hand side). A calculation of the peroxide consumption alone shows that it decreases with increasing oxygen concentration (broken lines a' to d'). The continuous curves (a to d) illustrate the total consumption of peroxide and oxygen based on the amount of polyethylene formed which increases with the total amount of initiator added.

The graph on the right-hand side of Fig. 6 shows the peroxide consumption in the polymerization reaction initiated by di-tert-butyl peroxide alone. A comparison of Curves e (Fig. 6, graph on the right-hand side) for 10 mol ppm di-tert-butyl peroxide with Curves a' to d' (Fig. 6, left-hand side) for 10 mol ppm peroxide in the presence of 6 mol ppm (curve a') and 60 mol ppm (Curve d') oxygen, respectively, shows the participation of oxygen in the initiation of the polymerization reaction.

Finally, the amount of polyethylene formed at elevated temperatures in the presence of oxygen can be compared with conversion following initiation by peroxide or oxygen alone. The graph on the left-hand side of Fig. 7 illustrates the conversion following initiation with 10 mol ppm di-tert-butyl peroxide in the absence of oxygen (Curve a), in the presence of 37 mol ppm oxygen (Curve b), and with 37 mol ppm oxygen alone (Curve c), plotted as a function of the polymerization temperature. The broken line d is obtained by adding together the conversions from the polymerization processes initiated only with peroxide and oxygen respectively. A much lower level of conversion is obtained from the simultaneous addition of the same quantities of peroxide and oxygen. The result is the same when tert-amyl perneodecanoate is used (right-hand graph, Fig. 7). Although oxygen acts as an initiator at elevated temperatures ($T > 160^{\circ}\text{C}$), it seems to simultaneously inhibit the peroxide-initiated polymerization of ethylene.

No such effect was observed on addition of oxygen alone. As expected, the conversion obtained from the oxygen-initiated polymerization increases with the root of the oxygen concentration.

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