Effectiveness of Organic Peroxide Initiators in the High-Pressure Polymerization of Ethylene

Gerhard Luft[a]; Helmut Bitsch[a]; Hans Seidl[b]

[a] Institut für Chemische Technologie Technische Hochschule Darmstadt, Germany [b] Peroxidchemie GmbH Höllriegelskreuth, Germany

PLEASE SCROLL DOWN FOR ARTICLE

Effectiveness of Organic Peroxide Initiators in the High-Pressure Polymerization of Ethylene

GERHARD LUFT and HELMUT BITSCH

Institut für Chemische Technologie
Technische Hochschule
Darmstadt, Germany

and

HANS SEIDL

Peroxidchemie GmbH
Höllriegelskreuth, Germany

ABSTRACT

The effectiveness of organic peroxides as initiators in the polymerization of high-pressure polyethylene has been studied in order to assess the most successful from a technical and economic view point. For this purpose polymerization experiments were carried out with ten different peroxides which are effective at various temperature ranges, e.g., 110 to more than 300°C. The organic peroxide consumption per kilogram of polyethylene produced was determined as a function of reaction temperature, pressure, organic peroxide concentration, and the mean residence time in the reactor. Also the dependence on the intensity of stirring inside the reactor was studied. The

organic peroxide consumption initially decreases with increasing
temperature, passes through a minimum, and then rises again.
The minimum organic peroxide consumption and the related
temperature are different for individual organic peroxides and
are greatly influenced by the reaction conditions. From a study
of the results, criteria to select the most suitable organic per-
oxide for certain reaction conditions including financial con-
siderations are put forward.

INTRODUCTION

The production of high-pressure polyethylene is carried out under
a wide range of reaction conditions so as to produce a variety of
products with good application and processing properties. To achieve
a high rate of conversion and reduce production costs, it is advisable
to initiate polymerization at as low a temperature as possible and to
have the temperature in the reactor as high as the decomposition
limit of the monomer allows [1]. For these reasons, in practice,
the reactors operate at temperatures between 130°C and almost
350°C, depending on the process.
    To cover this wide temperature range, organic peroxides dissolved
in hydrocarbons for metering purposes are used extensively as
polymerization initiators as well as oxygen. These organic peroxides
come in a variety of different forms and differ chiefly in their active
oxygen content and in their half-life temperature. Table 1 shows
organic peroxides used in the production of low-density polyethylene.
The half-life value given is a measure of the decomposition rate of
the organic peroxide at a definite temperature and thus provides a
suitable point of reference for selecting an organic peroxide for a
given polymerization temperature.
    However, a better criterion, which also takes into account finan-
cial considerations, is the quantity of initiator which must be utilized
to produce a unit of polyethylene. To measure the efficiency of the
initiator and to determine its dependence upon the nature of the
organic peroxide as well as on the polymerization conditions from
the point of view of process optimization, both technically and eco-
nomically, we have carried out experiments with different organic
peroxide initiators. Ten peroxides were used, differing widely in
their half-life characteristics. Dialkyl and diacyl peroxides,
peresters, and peroxydicarbonates were studied.

TABLE 1. Organic Peroxides Used in Production of Low-Density Polyethylene

Peroxide	Formula	Molecular weight	Form	Active oxygen content (% pure peroxide)	Temp. for half-life of 1 min (°C)
Isobutyryl peroxide	$\left[H\text{-}C \begin{smallmatrix} CH_3 \\ | \\ | \\ CH_3 \end{smallmatrix} \overset{O}{\overset{\|}{C}}\text{-}O \right]_2$	174.2	Solution in aliphatics	9.18	90
Isopropyl peroxi-dicarbonate	$\left[H\text{-}C \begin{smallmatrix} CH_3 \\ | \\ | \\ CH_3 \end{smallmatrix} \text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O \right]_2$	206.2	Solid	7.78	95
Di-n-butyl peroxydicarbonate	$\left[n\text{-}C_4H_9\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-} \right]_2$	234.3	Solution in aliphatics	6.83	90
Di-sec-butyl peroxydicarbonate	$\left[sec\text{-}C_4H_9\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-} \right]_2$	234.3	Solution in aliphatics	6.83	90

(continued)

TABLE 1 (continued)

Peroxide	Formula	Molecular weight	Form	Active oxygen content (% pure peroxide)	Temp. for half-life of 1 min (°C)
Dicyclohexyl peroxidicarbonate	$[C_6H_{11}-O-C(=O)-O-]_2$	286.3	Powder	5.60	90
Di-(2-ethylhexyl) peroxidicarbonate	$[C_4H_9-CH(C_2H_5)-CH_2-O-C(=O)-O-]_2$	346.5	Solution in aliphatics	4.62	90
tert-Butyl perneodecanoate	$i\text{-}C_9H_{19}-C(=O)-O-O-C(CH_3)_3$	246.4	Solution in aliphatics	6.50	100
tert-Butyl perpivalate	$(CH_3)_3-C-C(=O)-O-O-C(CH_3)_3$	174.2	Solution in aliphatics	9.18	110
Bis(3,5,5-trimethyl-hexanoyl) peroxide	$[i\text{-}C_8H_{17}-C(=O)-O-]_2$	314.5	Solution in aliphatics	5.09	115
Dioctanoyl peroxide	$[C_7H_{15}-C(=O)-O-]_2$	286.4	Powder	5.60	120

Didecanoyl peroxide	$\begin{bmatrix} O \\ \parallel \\ C_9H_{19}-C-O- \end{bmatrix}_2$	342.5	Powder	4.67	120
Dipropionyl peroxide	$\begin{bmatrix} O \\ \parallel \\ C_2H_5-C-O \end{bmatrix}_2$	146	Solution in aliphatics	10.96	115
Dilauroyl peroxide	$\begin{bmatrix} O \\ \parallel \\ C_{11}H_{23}-C-O- \end{bmatrix}_2$	398.6	Powder	4.00	120
tert-Butyl perisobutyrate	$\begin{matrix} CH_3 & O \\ \mid & \parallel \\ H-C-\!\!-C-O-O-C(CH_3)_3 \\ \mid \\ CH_3 \end{matrix}$	160.2	Solution in aliphatics	9.98	130
tert-Butyl per-2-ethylhexanoate	$\begin{matrix} O \\ \parallel \\ C_4H_9-CH-\!\!\!-C-O-O-C(CH_3)_3 \\ \mid \\ C_2H_5 \end{matrix}$	216.3	Liquid	7.38	130
tert-Butyl peracetate	$\begin{matrix} O \\ \parallel \\ CH_3-C-O-O-C(CH_3)_3 \end{matrix}$	132.2	Solution in aliphatics	12.1	160
tert-Butyl per-3,5,5-trimethylhexanoate	$\begin{matrix} O \\ \parallel \\ iso-C_8H_{17}-C-O-O-C(CH_3)_3 \end{matrix}$	230.3	Liquid	6.87	160

LUFT, BITSCH, AND SEIDL

TABLE 1 (continued)

Peroxide	Formula	Molecular weight	Form	Active oxygen content (% pure peroxide)	Temp. for half-life of 1 min (°C)
tert-Butyl perbenzoate	$C_6H_5-C-O-O-C(CH_3)_3$ with $\overset{O}{\underset{\|\|}{}}$	194.2	Liquid	8.24	170
Di-tert-butyl peroxide	$(CH_3)_3-C-O-O-C(CH_3)_3$	146.2	Liquid	10.90	190
tert-Butyl hydroperoxide	$(CH_3)_3 C-O-O-H$	90.1	Liquid	17.8	260[a]

[a]Determined on the pure product; commercially available products have substantially lower half-lives.
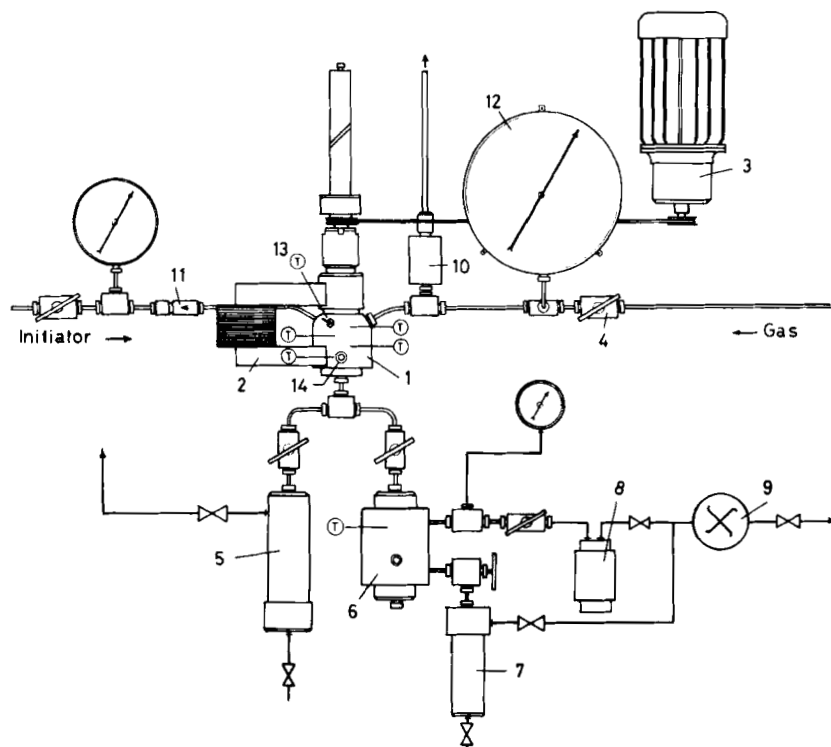
FIG. 1. Polymerization equipment (3000 bar, 350°C): (1) stirred tank reactor; (2) heating; (3) driver; (4) inlet valve; (5) separator; (6) high-pressure separator; (7) low-pressure separator; (8) wax separator; (9) flow meter; (10) rupture disk; (11) check valve; (12) manometer; (13) thermocouple; (14) sapphire window.

EXPERIMENTAL

Polymerization experiments were carried out in the laboratory with apparatus which operated continuously and contained all the features of a large-scale commercial plant (Fig. 1). The main component, the autoclave reactor, was equipped with an inductive heating system and a fast-running, magnetic-driven agitator. The autoclave is able to withstand pressures up to 3000 bar and temperatures up to 350°C. Two pressure-resistant sapphire windows were incorporated in the reactor

jacket to permit one to follow the polymerization visually and to as-
certain whether the reaction mixture is homogeneous or whether
phase separation takes place. Phase separation/homogeneity was
followed by means of a laser beam.

Before any polymerization experiments could proceed, the entire
apparatus was carefully evacuated and the stirred tank reactor heated
to the required reaction temperature. Ethylene was brought up to the
reaction pressure by means of a multi-stage diaphragm compressor
and then introduced into the reactor. The organic peroxide was dis-
solved in a toluene/n-heptane mixture at a concentration of 3 g/1000
cm^3 and fed directly into the ethylene inlet pipe by use of a metering
device developed in our laboratories; alternatively, it was mixed with
the compressed ethylene in a separate autoclave. This latter variation
was preferred for small amounts of organic peroxide because it meant
the initiator concentration could be adjusted more accurately. In the
reactor it was found that up to 35% conversion of ethylene to poly-
ethylene could occur under constant conditions of pressure, tempera-
ture, concentration, and residence time. The polymer formed was
separated from unconverted monomer by means of a pressure release
system to 150-300 bar or to normal pressure behind the outlet valve
in the reactor and was collected in two separators, one of which re-
ceived product until a steady state was attained. The pressure inside
the reactor and the high-pressure separator was measured manometri-
cally. The temperature of the ethylene feed was measured by means
of a sheathed thermocouple in the reactor inlet. In order to control
the temperature inside the reactor, four thermocouples of 0.5 mm
thickness were adjusted near the shaft of the stirrer and one thermo-
couple was placed near the wall of the jacket. Gas currents were also
measured entering and leaving the reactor, and the quantity of organic
peroxide metered into the reactor. The concentration of the organic
peroxide solution was determined iodometrically [2]. The polymer,
which was formed as a pulp or flocks, depending on the separation
pressure, was removed from the separators at the end of the poly-
merization and weighed.

The polymerization experiments were carried out with a mean
residence time of 65 sec and a pressure of 1700 bar (kept constant by
suitable regulating devices) and in a temperature range from 110 to
340°C. The organic peroxide concentration in the ethylene entering
the reactor was 225 to 579 ppm, depending upon the molecular weight
(Table 2), and this corresponds to molar concentration of 40 ppm
on the average.

In order to investigate the influence of the initiator concentration,
residence time, and reaction pressure on polymerization efficiency,
a further series of tests with dioctanoyl peroxide as the initiator were

TABLE 2. Peroxides Studied

No.	Peroxide	Molecular weight	Concentration in the commercially available form (% by wt)	Concentration in ethylene (ppm by wt)	
				Commercial form	100% Peroxide
Peresters					
I	tert-Butyl per(2-ethyl)-hexanoate	216.3	98.5	357	352
III	tert-Butyl perpivalate	174.2	74.8	380	284
VII	tert-Butyl perneodecanoate	246.4	98.5	365	360
VIII	tert-Butyl per-3,5,5-tri-methylhexanoate	230.3	99.5	329	327
IX	tert-Butyl perbenzoate	194.2	99.7	256	255
Diacyl peroxides					
II	Di isononanoyl peroxide	314.5	74.6	633	472
IV	Dilauroyl peroxide	398.6	98.7	587	579
V	Dioctanoyl peroxide	286.4	98.6	431	425
Dialkylperoxide					
X	Di-tert-butyl peroxide	146.2	99.5	220	221
Peroxydicarbonate					
VI	Di-cyclohexylpercarbonate	286.3	98.9	420	415

carried out. The initiator concentration was decreased in stages from
420 ppm (standard value) to 85 ppm, the residence time reduced by
increasing the throughput from 65 to 12 sec, and the pressure varied
between 1100 and 2000 bar. The influence of the intensity of the
stirring was studied by varying the speed of the stirrer between 110
and 1000 rpm.

RESULTS AND DISCUSSION

Variation of Temperature

The results obtained from the measurements carried out in a
typical polymerization are shown in Fig. 2. Figure 2a shows conver-
sion as determined from the amount of polyethylene formed per unit
time and ethylene used plotted against reaction temperature. When
the initial organic peroxide concentration is kept constant, the conver-
sion rises sharply at first with temperature, passes through a maxi-
mum, and then decreases again (Fig. 2a).
The initiator consumption in grams per kilogram of polyethylene
produced was calculated from the polyethylene formed and the amount
of organic peroxide metered into the reactor; this was plotted against
reaction temperature as a criterion for polymerization efficiency
(Fig. 2b). The specific initiator consumption drops sharply as the
reaction temperature rises, only to increase again. The tempera-
ture at which a minimal quantity of initiator is required, i.e., at
which the peroxide reaches its greatest polymerization efficiency,
is considered to be the optimal reaction temperature.

Initiator Concentration

The polymerization efficiency depends not only on the temperature
in the reactor but also on other reaction conditions. When the initiator
concentration in the ethylene entering the reactor decreases from
420 ppm to 250 or 85 ppm, the consumption of dioctanoyl peroxide
used drops from 3.1 to 1.1 g peroxide/kg polyethylene produced,
while the optimum temperature increases slightly (Fig. 3).

Residence Time

When the mean residence time is reduced from 65 sec (selected
as the standard value) to 12 sec, all other parameters (initiator
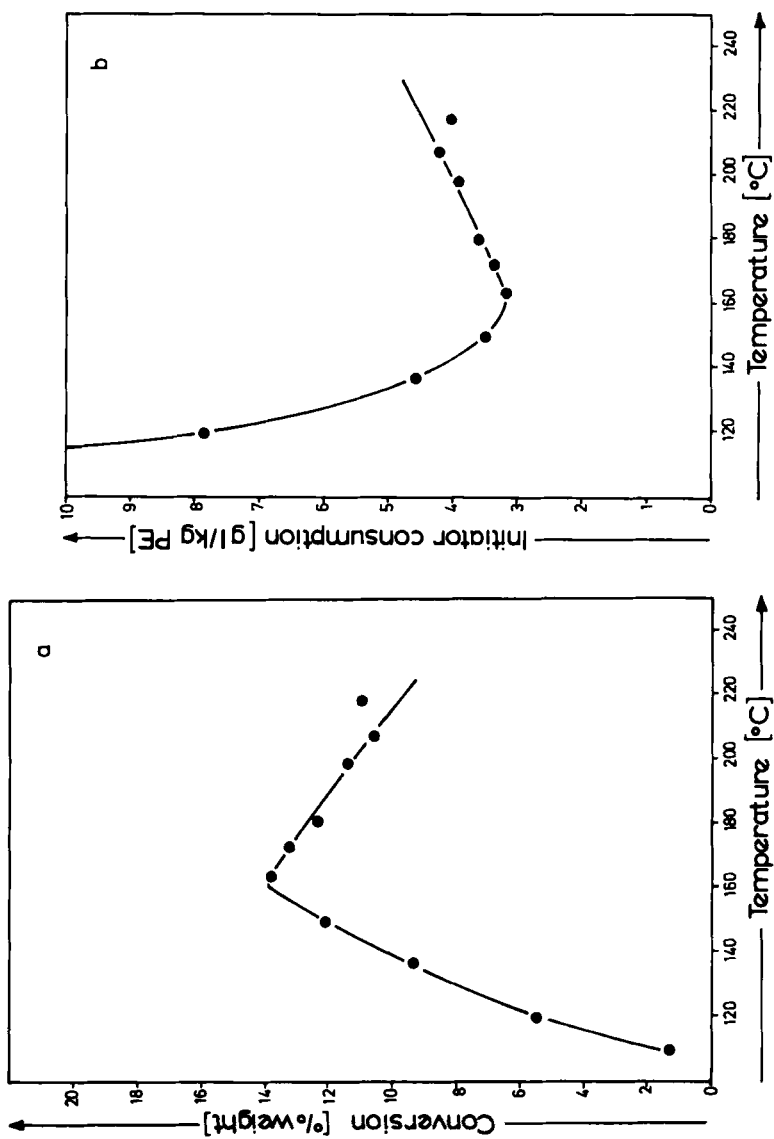
FIG. 2. Influence of the temperature on (a) conversion and (b) consumption of initiator. Initiator, dioctanoyl peroxide; mean residence time, 65 sec; pressure, 1700 bar; initiator concentration in the inlet, 420 ppm.
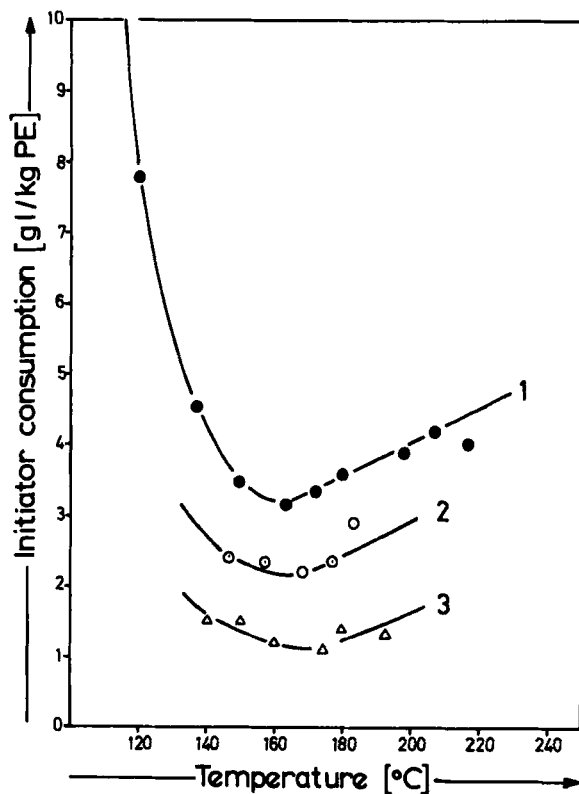
FIG. 3. Influence of the initiator concentration: (1) 420 ppm (by weight); (2) 250 ppm; (3) 85 ppm. Initiator, dioctanoyl peroxide; mean residence time, 65 sec; pressure, 1700 bar.

concentration 420 ppm, pressure 1700 bar) being constant the optimal temperature increases, and the specific organic peroxide consumption almost doubles (Fig. 4).

Pressure

The same tendency is evident: when the synthesis pressure drops from 1700 to 1100 bar, a sharp rise in the optimal polymerization temperature and in the initiator consumption is observed below
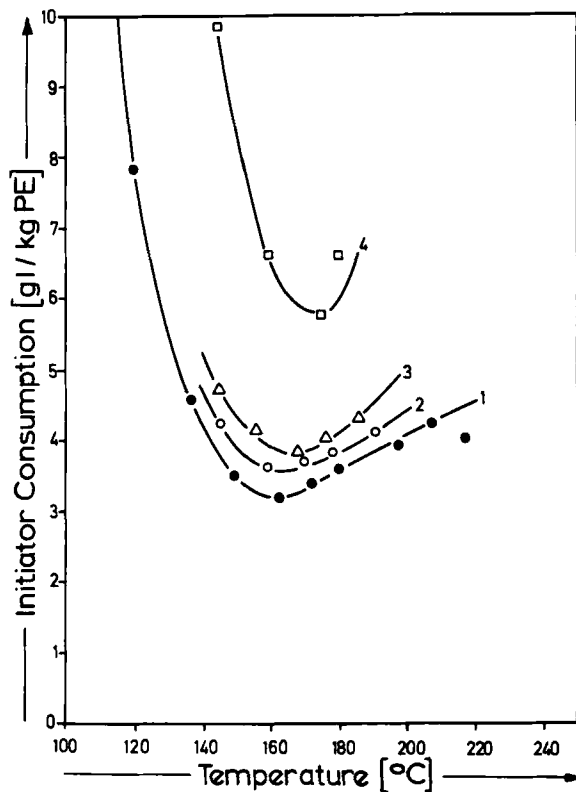
FIG. 4. Influence of the residence time: (1) 65 sec; (2) 38 sec; (3) 27 sec; (4) 12 sec. Initiator, dioctanoyl peroxide; pressure, 1700 bar; initiator concentration, 420 ppm.

1500 bar (Fig. 5). This can be attributed to the fact that a phase separation takes place [3, 4] in this pressure range, and this brings about a reduction in the polymerization rate because of the slow diffusion of monomer into the denser phase, which is rich in polyethylene and in which initiator is concentrated. At higher pressures, the influence of pressure decreases, particularly as regards the optimal reaction temperature as is shown in polymerization reactions carried out at a pressure of 2000 bar.

FIG. 5. Influence of the pressure on (a) minimum consumption of the initiator and (b) optimal temperature of polymerization. Initiator, dioctanoyl peroxide; mean residence time, 65 sec; initiator concentration, 420 ppm.

Intensity of Mixing

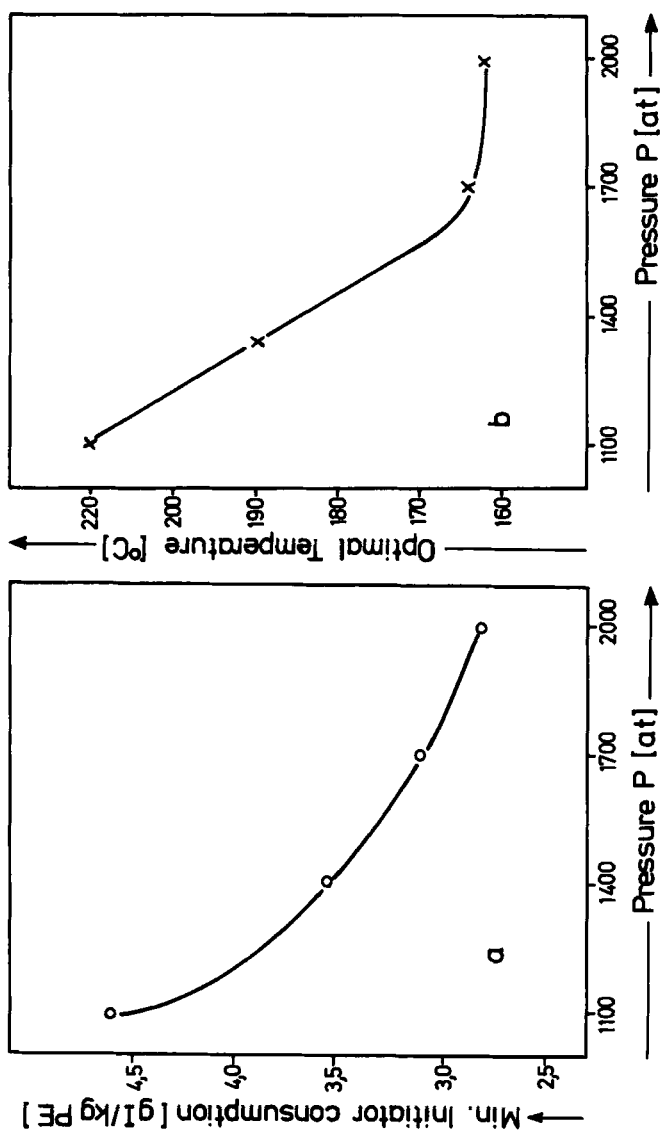As a consequence of insufficient mixing, temperature gradients can result which strongly influence the polymerization. In order to study this problem the speed of the stirrer was changed between 110 and 1000 rpm. At a low stirring velocity (110 rpm), steep temperature gradients were observed between the top of the reactor where the ethylene is introduced and the outlet on the bottom. The gradients were as high as 40°C with increasing conversion and unfavorable shape of the stirrer. With increasing speed of the agitator the temperature gradients lessened. At stirring speeds of 400 rpm the temperature is uniformly distributed inside the reactor, and measurements of the residence time distribution show the curve of an ideal mixed stirred tank reactor at velocities of 300 rpm. On going from low to high stirring speeds, the minimum initiator consumption also decreases as shown in Fig. 6 [5].
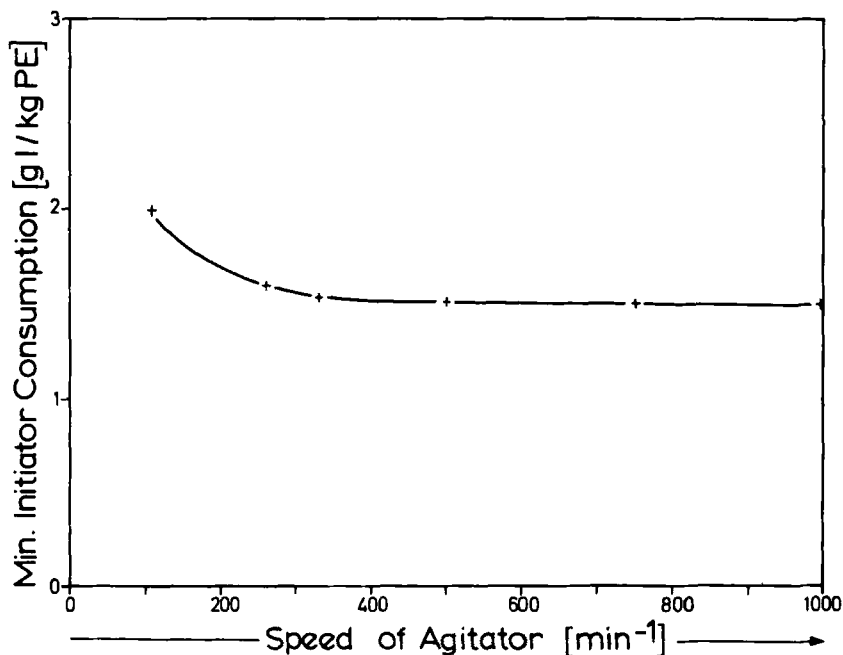

FIG. 6. Influence of the speed of the stirrer. Initiator, tert-butyl per(2-ethyl)hexanoate (I); initiator concentration, 315 ppm; mean residence time, 65 sec; pressure 1700 bar; mean temperature 175-185°C.
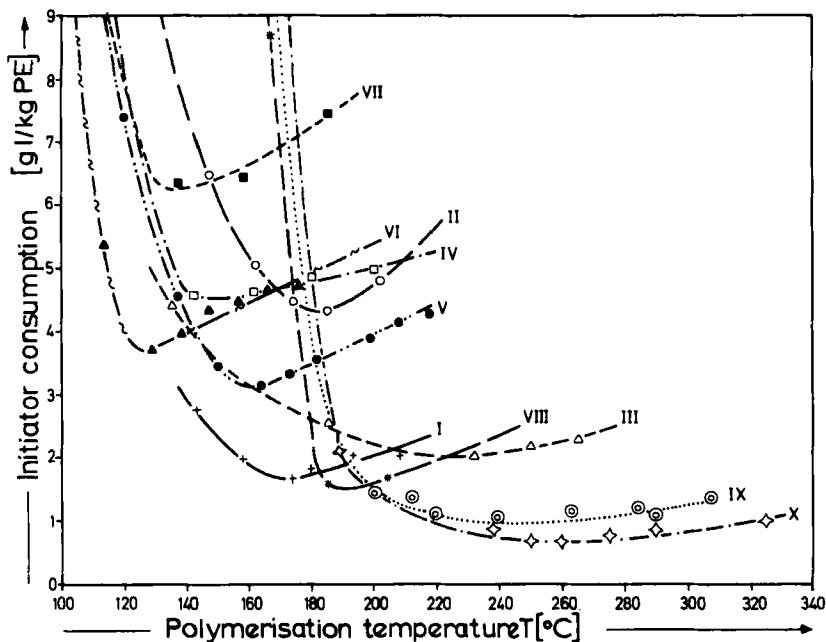
FIG. 7. Influence of the type of initiator: (I) tert-butyl per(2-ethyl)hexanoate (t-butyl peroctoate); (II) diisononanoyl peroxide; (III) tert-butyl perpivalate; (IV) dilauroyl peroxide; (V) dioctanoyl peroxide; (VI) dicyclohexyl percarbonate; (VII) tert-butyl perneodecanoate; (VIII) tert-butyl per-3,5,5-trimethylhexanoate (isononanoate); (IX) tert-butyl perbenzoate; (X) di-tert-butyl peroxide. Pressure, 1700 bar; mean residence time, 65 sec; initiator concentration 40 ppm (molar).

Initiator

Considerable differences in polymerization efficiency become evident when the individual organic peroxides are compared (Fig. 7). The initiator consumption varies between 0.7 and more than 6 g initiator/kg polyethylene. The differences remain, too, when the initiator consumption is related to the active oxygen content of the individual organic peroxide. Di-tert-butyl peroxide (X), tert-butyl perbenzoate (IX), and tert-butyl perisononanoate (VIII) as well as tert-butyl peroctoate (I) and tert-butyl perpivalate (III) proved to be

particularly efficient, with a specific consumption of 0.7 to 2 g initiator. In contrast, 6 g initiator/kg polyethylene is required with tert-butyl perneodecanoate (VII). The lowest optimal reaction temperature was measured with dicyclohexyl percarbonate (VI). The values for tert-butyl perneodecanoate (VII) and dilauroyl peroxide (IV) are somewhat higher, whereas tert-butyl perbenzoate (IX) and di-tert-butyl peroxide (X) show very high optimal reaction temperatures.

If one considers the progression of the curves produced, it is striking that the initiator consumption for the majority of organic peroxides drops steeply at first, reaches a minimum, and then as in the case of tert-butyl perneodecanoate (VII) or diisononanoyl peroxide (II) rises again at a moderate rate as the polymerization temperature increases. Similar types of curve are noted with tert-butyl perisononanoate (VII), and tert-butyl perbenzoate (IX), but after reaching a minimum the curve rises very slightly. For this reason these peroxides can only be used with good efficiency above the optimal reaction temperature. The broad curves for tert-butyl perpivalate (III) and particularly di-tert-butyl peroxide, however, indicate a good degree of polymerization efficiency in a wide temperature range. It is not possible to confirm the existence of a curve on which all consumption minima or all points showing maximum polymerization efficiency should lie, as was postulated in the literature [6, 7].

The shape of the initiator consumption-temperature curves also affects the reactor temperature, which is usually adjusted by the quantity of organic peroxide introduced into the system. If the operating conditions of the reactor lie below the optimal reaction temperature on a steep curve branch, then a slight reduction in the temperature in the reactor causes a rapid increase in the initiator consumption, and this then leads to a further decrease in the reactor temperature without any external intervention. Conversely, if the temperature increases, then the initiator consumption drops drastically, and the temperature then rises to the optimal operation temperature. This process bears a certain similarity with the extinction-ignition processes in heterogeneous catalytic reactions. When operating large-scale reactors, the steep curve branch will be avoided and work will be carried out at higher temperatures. Thus, a slight increase in the initiator consumption with increasing temperature will have a favorable effect on the reaction behavior. Organic peroxides with a wide initiator consumption temperature curve give the facility for the reactor to be operated below the optimal polymerization on the left hand curve branch.

KINETICS

The results obtained from our work on the initiator consumption vs temperature relationship can be described through the kinetics of polymerization and the mass balance relationship in the reactor. The simplified mechanism of peroxide-initiated polymerization, which encompasses initiator decomposition, formation, growth of chain radicals, and chain termination is shown in Eqs. (1)-(4).

Initiator Decomposition:

$$I \xrightarrow{k_I} 2 \, R\cdot \tag{1}$$

Chain Radical Formation:

$$R\cdot + M \xrightarrow{k_W} R \tag{2}$$

Growth:

$$R_i + M \xrightarrow{k_W} R_{i+1} \tag{3}$$

Termination:

$$R_i + R_j \xrightarrow{k_A} P_{i+j} \tag{}$$

$$\xrightarrow{} P_i + P_j \tag{4}$$
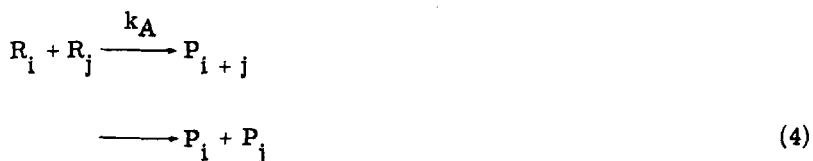
Equations for the change of the concentration of initiator, radicals, monomers, and polymers can thus be formed.

$$d[I]/dt = -k_I[I] = r_I \tag{5}$$

$$d[R]/dt = 2 k_I[I] - k_A[R]^2 = r_R \tag{6}$$

$$d[M]/dt = - k_w[R][M] = r_M \tag{7}$$

$$d[P]/dt = - k_A[R]^2 = r_P \tag{8}$$

The reactor mass balance for initiator and monomer are thus:

$$0 = (1/\tau)([I] - [I_0]) + r_I \tag{9}$$

$$0 = (1/\tau)([M] - M_0]) + r_M \tag{10}$$

Here $[I]$ and $[M]$ are the concentrations of initiator and monomer in the reactor; $[I_0]$ and $[M_0]$ are the corresponding values at the reactor entrance. τ is the mean residence time, and r_P, r_R, r_I, r_M are reaction rates. These equations apply provided that the reactor, like the agitator vessel used, is thoroughly mixed to an ideal degree and does not have concentration or temperature gradients.

Using Bodenstein's theorem, the radical concentration can be calculated from Eq. (6) to give:

$$[R] = \sqrt{2k_I[I]/k_A} \tag{11}$$

The unknown initiator concentration in the reactor comes from Eqs. (9) and (5) and is:

$$[I] = [I_0]/(1 + \tau k_I) \tag{12}$$

For polymers it is advisable to introduce the weight g instead of the molar concentration. The density of the reaction mixture ρ and the molecular weight of the initiator M_I, gives the relationship for the weight g_P in the polymer formed or for the specific initiator consumption η from Eqs. (5)-(12)

$$g_P = \left[\frac{1}{k'} \sqrt{\frac{M_I}{2 g_{I_0} \rho \tau}} \left(\frac{1}{\tau k_I} + 1 \right) + 1 \right]^{-1} \tag{13}$$

$$\eta = g_{I_0}/g_P$$

$$= g_{I_0}\left[\frac{1}{k'}\ \sqrt{\frac{M_I}{2g_{I_0}\rho\tau}\left(\frac{1}{\tau k_I}+1\right)}+1\right] \qquad (14)$$

where

$$k' = k_w/\sqrt{k_A} \qquad (15)$$

The dependence of the velocity constant upon temperature and pressure is taken into account [8] through the relationship (16):

$$k = k^\circ\ \exp\ \{-[E + \Delta v^*(p - p_0)]/RT\} \qquad (16)$$

in which E represents the activation energy and Δv^* the activation volume of the individual partial stages in polymerization.

Equations (13) and (14) deduced can be used to interpret the various parameters upon polymerization conditions. For this purpose the equations have been simplified and at low polymerization temperatures $\tau k_I \ll 1$; hence,

$$g_P = k'\sqrt{k_I}\ \sqrt{2g_{I_0}\rho\tau^2/M_I} \qquad (17)$$

$$\eta = (1/k'\sqrt{k_i})\ \sqrt{M_I g_{I_0}/2\rho\tau^2} \qquad (18)$$

and for sufficiently high temperatures, where $\tau k_I \gg 1$, by analogy,

$$g_P = \left[(1/k')\ \sqrt{M_I/2\,g_{I_0}\rho\tau}+1\right]^{-1} \qquad (19)$$

$$\eta = g_{I_0}\left[\frac{1}{k'}\ \sqrt{M_I/2g_{I_0}\rho\tau}+1\right] \qquad (20)$$

As the difference in the activation energies in the growth and termination stages is $(E_w - E_a)/2 = 23 \times 10^3$ J/mole [9, 10] and the initiator decomposition shows a high activation energy $E_I = 100 - 170$ $\times 10^3$ J/mole, the rate constants k' and k_I increase with temperature. Accordingly the initiator consumption, from Eq. (18), at lower temperatures must decrease rapidly as the temperature rises. This was in fact observed in our experiments (Fig. 2). In the case of organic peroxides which have a small decomposition activation energy, such as tert-butyl perpivalate ($E_I = 109 \times 10^3$ J/mole) the initiator consumption changes less sharply with temperature (Fig. 7, curve III).

As was found in our measurements (Figs. 3 and 4), the initiator consumption increases with initial initiator concentration by the factor $g_{I_0}^{1/2}$ [low polymerization temperature, Eq. (18) to g_{I_0} [high temperature, Eq. (20)] and decreases in proportion to the residence time τ [Eq. (18)] or $\tau^{1/2}$ [Eq. (20)].

The reaction pressure influences the initiator consumption both by the density of the reaction mixture and the velocity constant. The influence of the density is unambiguous; initially it increases sharply with increasing pressure and then less because of reduced compressibility. Therefore, as the results in Fig. 5 show, the initiator consumption becomes smaller as the pressure increases. As the activation volumes of chain growth and termination are of equal size and are negative (-15 to -20 cm³/mole) the value

$$k' = (k_w^\circ / \sqrt{k_A^\sigma}) \exp \left\{ - [(E_w - E_A/2) + (\Delta v_w^* - \Delta v_A^*/2) (p - p_0)]/RT \right\}$$

increases with pressure, and the initiator consumption must decrease at high temperature according to Eq. (20). At low reaction pressure, the dependence of the decomposition constant k_I upon pressure is still a factor [Eq. (18)]. Because of the positive activation volume of 6 cm³/mole [4] on the average, k_I increases as the reaction pressure increases and modifies the influence of k' and ρ. This in turn reduces the initiator consumption.

The influence of stirring can be explained by a simple consideration. At low stirrer speed the reactor may be divided into two zones, having temperatures T_1 (e.g., 130°C) and T_2 (150°C). The initiator consumption in the two zones according to Fig. 2b is η_1 (5.5 gI/kg PE) and η_2 (3.5 gI/kg PE) and the total is $\eta_{1,2} = (\eta_1 + \eta_2)/2$ (4.5 gI/kg PE). If at high velocities of the agitator the temperature inside the reactor

is uniform $\overline{T} = (T_1 + T_2)/2$ (140° C), the initiator consumption from
Fig. 2b is lower ($\eta_{\overline{T}}$ = 4.25 gI/kg PE).

CHOICE OF ORGANIC PEROXIDE

The most suitable initiators for a given polymerization tempera-
ture were selected by use of the comsumption-temperature curves
(Figs. 3-7). The initiator should be adjusted to the reaction conditions
in such a way that the operational point of the reactor lies on the con-
sumption curve on or above the optimal polymerization temperature.
Organic peroxides which have a wide consumption curve, i.e., those
whose polymerization efficiency is less dependent upon tempera-
ture, are preferred, because they can be used over a wider tempera-
ture range and diminish the reactor's sensitivity. If there are marked
temperature profiles in a reactor [e.g., in a tubular reactor, a slim
agitator vessel with low axial mixing or in a multichamber agitator
vessel], then it is recommended that two or more organic peroxides
which are effective at different temperature ranges, selected on
the basis of the above criteria, be used.

It has been shown that the consumption of organic peroxides
measured in our evaluation is very consistent with the quantity of
initiator used per kilogram of polyethylene produced in large-scale
polymerization. Actual operational experience has confirmed the
dependences found upon initial peroxide concentration, the residence
time, and reaction pressure. To some extent, the actual polymeriza-
tion temperature is higher in practice, and the reactor dimensions
and mixing of reactants play an important part here. Thus, it has
been observed that organic peroxide consumption increases at a low
stirrer speed and that it is higher in reactors which have a large
length/internal diameter ratio.

As the prices of individual organic peroxides vary a great deal,
the price must also be taken into account along with consumption
and reaction progress when selecting an organic peroxide. Figure 8
shows costs of organic peroxides. The high cost for tert-butyl
perneodecanoate (VII) results because of its high consumption and
relatively high price. Perdicarbonates and tert-butyl perpivalate
should be the preferred initiators for low-temperature polymeriza-
tions. For medium to high polymerization temperatures, organic
peroxides such as tert-butyl peroctoate, tert-butyl perbenzoate, and
di-tert-butyl peroxide, which are relatively inexpensive, are recom-
mended. When diacyl peroxides such as nonanoyl peroxide or
octanoyl peroxide are used, somewhat higher specific consumptions
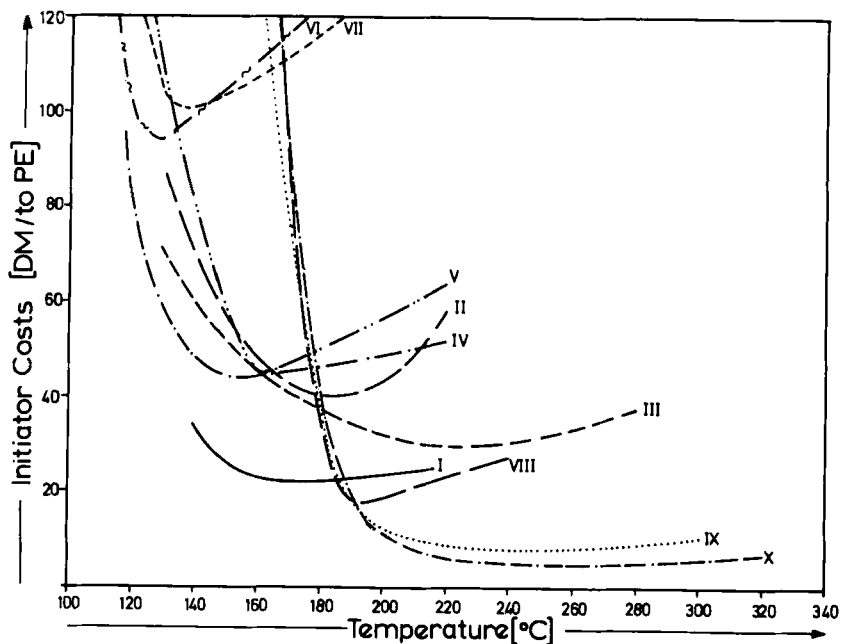must be allowed for.

FIG. 8. Costs of initiator: (I) tert-butyl per(2-ethyl)hexanoate
(tert-butyl peroctoate); (II) diisononanoyl peroxide; (III) tert-butyl
perpivalate; (IV) dilauroyl peroxide; (V) dioctanoyl peroxide;
(VI) dicyclohexyl percarbonate; (VII) tert-butyl perneodecanoate;
(VIII) tert-butyl per-3,5-5-trimethylhexanoate (isononanoate);
(IX) tert-butyl perbenzoate; (X) di-tert-butyl peroxide. Basis, 1976;
pressure 1700 bar; mean residence time, 65 sec; initiator concen-
tration, 40 ppm.

The solubility of organic peroxides, possible unpleasant aroma,
and problems of technical safety must also be considered when
selecting an organic peroxide. Organic peroxides which dissolve
readily require smaller quantities of solvent, so that metering in-
struments may be smaller and hence cheaper. The organic peroxide
must not precipitate or crystallize under high pressure in the feed
piping. There are crystallization problems with tert-butyl perbenzoate,
and hence tert-butyl perisononanoate is often used. Powdered organic
peroxides are generally less readily soluble, and this is why dilauroyl
peroxide has been replaced by the more readily soluble dioctanoyl
peroxide and which is effective in the same temperature range. The

peresters examined, tert-butyl peroctoate and tert-butyl perisonon-
anoate are being used more and more in place of tert-butyl periso-
butyrate and tert-butyl peracetate, which have an unpleasant aroma.

Safety considerations also limit the choice of organic peroxides.
Highly active peresters, like tert-butyl perneodecanoate, have to be
stored and transported below -5°C due to their low self-accelerating
decomposition temperature [11] and have to be delivered in 75%
solutions in aliphatic hydrocarbons. More stable peresters, like tert-
butyl perbenzoate and tert-butyl perisononanoate are sold commer-
cially in the pure form and can be stored without any cooling pre-
caution. The highly stable dicyclohexyl peroxydicarbonate can be
stored as a powder up to +5°C; organic peroxides in the solid form
are generally more stable than liquids.

Many factors therefore determine the choice of an organic
peroxide in the high pressure ethylene polymerization. As a con-
sequence a broad range of organic peroxides is still used industrially
as expressed in Table 1.

REFERENCES

[1]   G. Luft, CZ-Chemie-Technik, 2, 89 (1973).
[2]   Technical Bulletin, Peroxid-Chemie GmbH, Höllriegelskreuth,
      Germany.
[3]   R. Steiner and K. Horle, Chem.-Ing. Tech., 44, 1010 (1972).
[4]   G. Luft and A. Lindern, Angew. Makromol. Chem., 56, 99
      (1976).
[5]   W. Liebner, Thesis, Darmstadt.
[6]   Th. J. Van der Molen and C. Van Heerden, paper presented
      at Symposium on Chemical Reaction Engineering, Washington,
      1970.
[7]   Th. J. Van der Molen, J. Polym. Sci. Polym. Symp. Ed., 42,
      29 (1973).
[8]   R. Steiner and G. Luft, Chem. Eng. Sci., 22, 119 (1967).
[9]   G. Luft and R. Steiner, Chemiker-Z., 95, 11 (1971).
[10] P. Ehrlich and G. A. Mortimer, Fortschr. Hochpolym. Forsch.,
      7, 386 (1970).
[11] Peroxid-Chemie GmbH, Sicherheit beim Umgang mit organischen
      Peroxiden, Technical Bulletin, Höllriegelskreuth, 1976.