Peroxides as Initiators for High-Pressure Polymerization

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ABSTRACT

On the basis of the high-pressure polymerization of ethylene, in which organic peroxides are increasingly used as initiators, the problems which play an important part in selecting the most suitable initiators are discussed. Starting from the rate of decomposition of the initiator at the actual conditions of the high-pressure polymerization, the consumption of the initiators and its costs as well as its influence on the process control are considered. A second important point is the influence of the initiator on the properties of the polymer which can be exerted by the reaction of the initiator or its decomposition products with the polymer and the polymer chain radicals or the initiator decomposition products and residual initiator which remains dissolved in the polymer. The last part is devoted to the handling of peroxides during storage and metering in the reactor which are

questions of process technology and safety techniques. The
criteria discussed in respect to the choice of peroxidic initia-
tors are illustrated by two concrete examples, the synthesis of
low-density polyethylene in a triple chamber autoclave and in a
tubular reactor with multiple feed.

INTRODUCTION

Organic peroxides were first produced in substantial quantities
at the turn of the century as bleaching agents. Since then their usage
as bleaches has diminished, and today they are used as radical initia-
tors and, to a lesser extent, as oxidizing agents in organic syntheses.
    The main field of application is the plastics sector where peroxides
are used because of their ability to decompose easily into radicals
for the cross-linking of polyolefins and elastomers, as curing agents
for unsaturated polyesters, for the degradation of polymers, and in
particular as initiators for radical chain polymerizations [1, 2].
    In the plastics field in particular, the peroxide requirement has
increased many times in the last few years as a result of the increas-
ing demand for plastics. Approximately 6000 t of peroxides are
required worldwide in the production of high-pressure polyethylene
alone, the most important polymer from the quantitative point of
view. This quantity includes 10 to 20 different compounds which are
marketed in different commercial grades as liquids or in powder
form. Is this variety necessary, what are the properties required
of peroxidic initiators, and what criteria are the determining
factors for their selection?
    In order to be able to discuss these questions from a practical
point of view, the high-pressure polymerization of ethylene, in which
organic peroxides are increasingly used as initiators should be con-
sidered (Fig. 1). In this process the ethylene feed, together with
recycled unreacted ethylene from the polymerization stage, is sub-
jected to pressures of 1500 to 3000 bar before introduction into the
polymerization reactor [3, 4]. The peroxidic initiators are dissolved
in or diluted with suitable hydrocarbons and stored at temperatures
of +25 to -20°C in order to prevent premature decomposition. They
are then either metered directly into the reactor by means of pumps
or other conveying equipment or mixed with the compressed ethylene
in a concentration of 20 to 600 ppm by weight, upstream of the reactor.
    The subsequent polymerization can be carried out in tubular re-
actors or stirred autoclaves as well as in cascades of autoclaves.
These reactors differ widely in residence times as well as in con-
centration and temperature distributions. The temperatures used
are in the range of 130 to 350°C. This wide temperature range is
due in part to the heat of polymerization generated, which is largely
absorbed by the reaction mixture. However, the variation in tempera-
ture is necessary to obtain polymers of differing properties. For
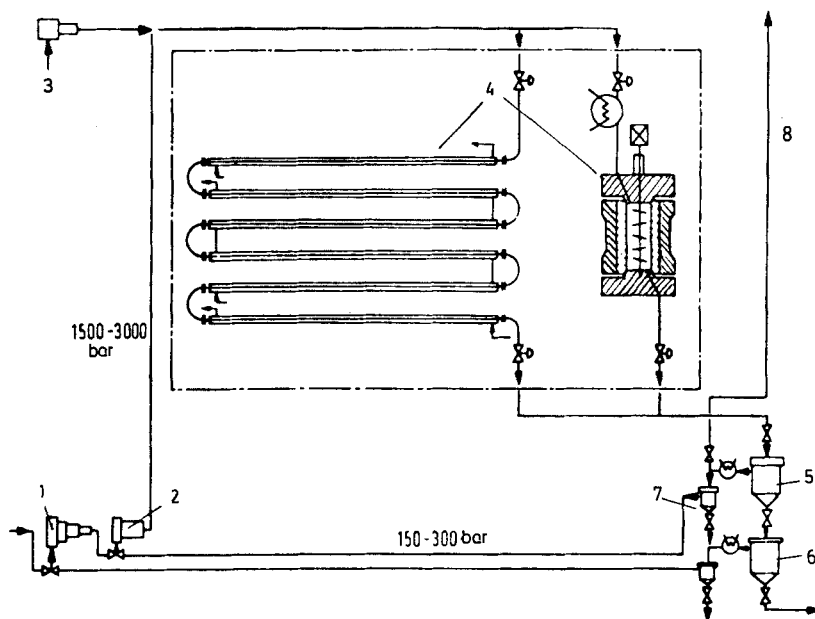
FIG. 1. Flow sheet of ethylene high-pressure polymerization. (1) Low-pressure compressor. (2) High-pressure compressor. (3) Initiator and modifier. (4) Tubular or autoclave reactor. (5) High-pressure separator. (6) Low-pressure separator. (7) Wax separation. (8) Discharge.

economic reasons not given here, the temperature difference between the reactants inside the reactor and those entering should be as large as possible.

On the basis of the above details, three different problem areas can be defined which play an important part in selecting the peroxide initiator: The first comprises the actual polymerization process, in which the rate of decomposition of the initiator, its consumption and costs, as well as its influence on the process control have to be taken into consideration. The second concerns the possible effect of the initiator on the polymer properties, and the third the handling, e.g., metering and storing of peroxides.

TABLE 1. Organic Peroxide Initiator in the High-Pressure Polymerization of Ethylene

Peroxide	Formula	Molecular weight	Form	Temp. for half-life of 1 min ($^\circ$C)
Isobutyryl peroxide		174.2	Solution in aliphatics	90
Isopropyl peroxidicarbonate		206.2	Solid	95
Di-n-butyl peroxydicarbonate	$[\, n\text{-}C_4H_9\text{-}O\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\text{-}]_2$	234.3	Solution in aliphatics	90
Di-sec-butyl peroxydicarbonate	$[\, sec\text{-}C_4H_9\text{-}O\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\text{-}]_2$	234.3	Solution in aliphatics	90
Dicyclohexyl peroxidicarbonate		286.3	Powder	90
Di-(2-ethylhexyl) peroxidicarbonate	$[\, C_4H_9\text{-}\overset{\overset{\textstyle C_2H_5}{\|}}{CH}\text{-}CH_2\text{-}O\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\,]_2$	346.5	Solution in aliphatics	90
tert-Butyl perneodecanoate	$i\text{-}C_9H_{19}\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\text{-}O\text{-}C(CH_3)_3$	246.4	Solution in aliphatics	100
tert-Butyl perpivalate	$(CH_3)_3\text{-}C\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\text{-}O\text{-}C(CH_3)_3$	174.2	Solution in aliphatics	110
Bis(3,5,5-trimethyl-hexanoyl) peroxide	$[\, i\text{-}C_8H_{17}\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}O\,]_2$	314.5	Solution in aliphatics	115

TABLE 1 (continued)

Peroxide	Formula	Molecular weight	Form	Temp. for half-life of 1 min (°C)
Didecanoyl peroxide	$\begin{matrix} O \\ \| \\ [\,C_9H_{19}-C-O-]_2 \end{matrix}$	342.5	Powder	120
Dilauroyl peroxide	$\begin{matrix} O \\ \| \\ [\,C_{11}H_{23}-C-O-]_2 \end{matrix}$	398.6	Powder	120
tert-Butyl perisobutyrate	$\begin{matrix} CH_3\ \ O \\ \|\ \ \ \ \ \| \\ H-C-\!-\!-C-O-O-C(CH_3)_3 \\ \| \\ CH_3 \end{matrix}$	160.2	Solution in aliphatics	130
tert-Butyl per-2-ethylhexanoate	$\begin{matrix} O \\ \| \\ C_4H_9-CH-\!-\!-C-O-O-C(CH_3)_3 \\ \| \\ C_2H_5 \end{matrix}$	216.3	Liquid	130
tert-Butyl peracetate	$\begin{matrix} O \\ \| \\ CH_3-C-O-O-C(CH_3)_3 \end{matrix}$	132.2	Solution in aliphatics	160
tert-Butyl per-3,5,5-trimethylhexanoate	$\begin{matrix} O \\ \| \\ iso-C_8H_{17}-C-O-O-C(CH_3)_3 \end{matrix}$	230.3	Liquid	160
tert-Butyl perbenzoate	$\begin{matrix} O \\ \| \\ C_6H_5-C-O-O-C(CH_3)_3 \end{matrix}$	194.2	Liquid	170
Di-tert-butyl peroxide	$(CH_3)_3-C-O-O-C(CH_3)_3$	146.2	Liquid	190
tert-Butyl hydroperoxide	$(CH_3)_3\ C-O-O-H$	90.1	Liquid	260

POLYMERIZATION INITIATION

Rate of Decomposition

Peroxides are particularly suitable as initiators for polymerization reactions because they readily undergo thermal decomposition to form radicals. As a rule, primary radicals are formed by homolytic cleavage of the O–O bond. These radicals initiate polymerization by reaction with the monomer:

$$R–O–O–R \longrightarrow 2R–O^\cdot$$

$$R–O^\cdot + M \longrightarrow R_1^\cdot$$
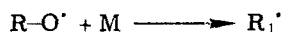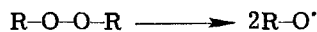
For this purpose, a sufficient quantity of radicals needs to be available; in other words, the rate of decomposition of the initiator must be adjusted to the rate of the subsequent polymerization stages and the residence time of the substances in the polymerization reactor. The decomposition half-life time $t_{1/2}$, which is inversely proportional to the rate of decomposition, is used to quantify this, short half-life times corresponding to high rates of decomposition and vice versa. In practice, the decomposition half-life under polymerization conditions should be 2 powers of 10 less than the mean residence time, i.e., $t_{1/2}$ should be in the region of 1 to 0.1 sec.

To fulfill this condition, peroxides with different activities are needed for use at different polymerization temperatures. Table 1 illustrates a number of commercially available peroxides suitable for high-pressure polymerization. These include peroxydicarbonates, such as dicyclohexyl peroxidicarbonate; peresters, such as t-butyl perneodecanoate or t-butyl perpivalate; diacyl peroxides, such as didecanoyl or dilauroyl peroxide; dialkyl peroxides, of which the best-known is di-t-butyl peroxide; and hydroperoxides, e.g., t-butyl hydroperoxide or tetramethyl butane hydroperoxide, not illustrated here. The peroxides are arranged according to their decomposition half-lives, measured as the temperature at which the half-life is 1 min. In practice this is the parameter by which peroxides are selected. A high temperature for a half-life of 1 min indicates that the peroxide is relatively stable and therefore suitable as an initiator for polymerization at high temperatures.

One particular problem lies in the fact that the values indicated were determined by measurements at normal pressure and usually at only moderately high temperatures, i.e., far from the actual high-pressure polymerization conditions. In order to eliminate this source of error, we have started to investigate peroxide decomposition under high pressures of up to 3000 bar and simultaneously high temperatures of up to 230°C. The difficulties encountered in the investigation of
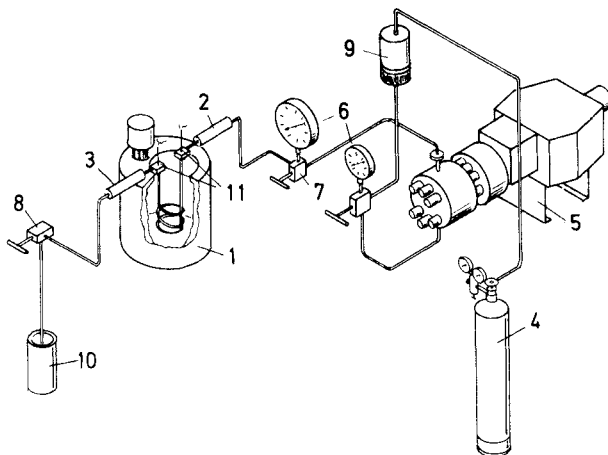
FIG. 2. Flow-tube equipment. (1) Thermostat with capillary tube. (2) Heater. (3) Cooler. (4) N_2 preliminary pressure. (5) High-pressure pump. (6) Manometer. (7) Inlet valve. (8) Discharge valve. (9) Storage vessel. (10) Sampling site. (11) Thermocouple.

peroxide decomposition under high pressure are due to the high-compression stress on the equipment, which requires special design and highly resistant materials, and particularly to the rapid rates of reaction at high temperatures. While at moderate temperatures the half-lives are of the order of a few minutes to some hours, so that sufficient time is available for sampling and the tests can be carried out batchwise, at high temperatures it is necessary to resort to indirect concentration measurements and flow processess because of the very brief half-life times of seconds and tenths of seconds.

In the flow process which we have developed as a standard method [5], the peroxide solution is introduced continuously by means of a high-pressure diaphragm pump into a thermostatted capillary tube (Fig. 2) in which the decomposition reaction takes place under steady conditions.

From this tubular reactor a needle valve is used to relieve the pressure of the solution to normal. The solution is thoroughly cooled to freeze the reaction, and the residual peroxide is determined iodometrically. The reaction time may be altered by changing the pump output and the dimensions of the capillary tube, making it possible to determine half-lives ranging from 260 sec to the technically interesting region of 0.1 sec. The results of a decomposition experiment using t-butyl perpivalate are given in Fig. 3, where residual peroxide content is plotted as a function of reaction time. In this example, measurements were made at a temperature of 130°C at pressures between 1 and 3000 bar.
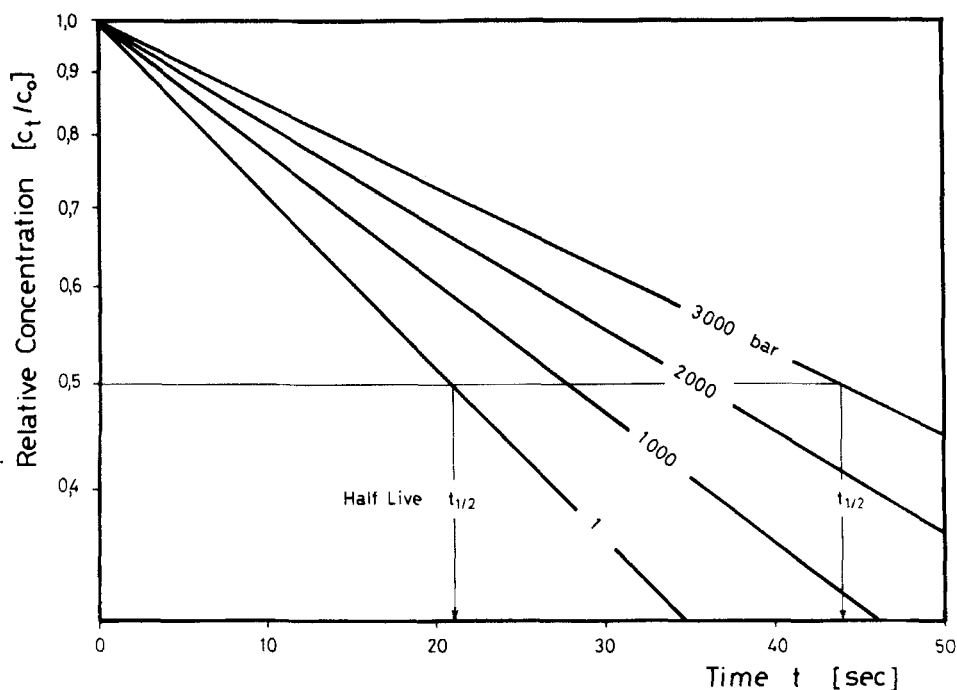
FIG. 3. Diagram of residual quantities/time. Initiator: t-butyl perpivalate. Solvent: i-dodecane. Concentration: 1% by weight. Temperature: 130°C.

The straight lines which are obtained in the semilogarithmic diagram for all the peroxides examined indicate that the decomposition is a first-order reaction even at high pressure. An induced decomposition, i.e., the reaction of the primary radicals formed by homolysis or of solvent radicals with the peroxide, is not noticeable at the low peroxide concentration in the temperature range examined.

The decomposition half-life increases greatly with increasing pressure, doubling with a pressure increase from normal to 3000 bar. Pressure therefore reduces the rate of decomposition. This can be explained by the increase in volume of the peroxide molecule in the transition state through the elongation of the O–O bond. The so-called activation volume, Δv^*, i.e., the difference between the volume of the transition complex formed during the decomposition and that of the initial state, is positive, so that the rate constant k of the decomposition reaction according to the equation

$$\frac{\partial (\ln k)}{\partial p} \Bigg|_T = -\frac{\Delta v^*}{RT}$$

will decrease with increasing pressure, as observed in the experiment.

The activation volumes (Table 2) of the peroxides examined, which have been determined experimentally, are between 4 and 13 cm^3/mole. Lower activation volumes were obtained for dicyclohexyl peroxydicarbonate and for t-butyl perpivalate and dioctanoyl peroxide, so for these products the effect of pressure on the rate of decomposition, and therefore on the half-life, is lowest. The figures for t-butyl perpivalate and dioctanoyl peroxide are identical; this means that the half-lives of both peroxides increase under pressure by the same factor. t-Amyl perpivalate and di-t-butyl peroxide, in particular, have higher activation volumes.

The large activation volumes can be explained by the fact that the molecules are bulkier, i.e., the groups adjacent to the O—O bond have a larger effective cross-section, so that a greater volume increase takes place on elongation of the O—O bond in the transition state. This is particularly evident in the case of the increase in the activation volume of the pivalic acid perester when a butyl group is substituted by an amyl group. Whereas the half-lives of both peroxides are approximately the same at normal pressure and identical temperature, the half-life of t-amyl perpivalate is greater than that of the butyl compound at high pressure.

The examples show that decomposition half-lives are much higher under high pressure, i.e., under polymerization conditions, and must always be taken into consideration when a peroxide is selected. It should also be taken into account that the effect of the pressure varies with individual peroxides depending on their structure. Peroxides with bulky, sterically hindered groups exhibit a stronger dependence on the half-life and the rate of decomposition on the pressure.

The activation energies, determined on the basis of the relation between decomposition and the temperature, increase in the sequence peresters, diacyl peroxide, dialkyl peroxide, from 102 to 152 kJ/mole, with the peresters differing only slightly from diacyl peroxide (and peroxidicarbonate). The chain length has hardly any influence on the activation energy. This result is obtained from a comparison between the two perpivalates, and can be regarded as confirmed by measurements carried out by other authors with diacyl peroxides at normal pressure.

The rate of decomposition of peroxides with a high energy of activation, for instance di-t-butyl peroxide, increases rapidly with temperature. They are therefore recommended for use within a narrow temperature range and for applications where it is necessary to avoid uncontrolled preliminary decomposition before the proper reaction temperature is reached; for example, where they are introduced into the reactor by means of heated lines or when they are incorporated into heated polyolefins, cross-linking of which is initiated by subsequent heating.

Peroxides with a low activation energy, such as peroxydicarbonates and perpivalates, are particularly suitable for use within a wide

TABLE 2. Decomposition Data of the Peroxides Investigated

|	Temperature for half-life time of 1 min (°C) at 1 bar	Temperature for half-life time of 1 min (°C) 3000 bar	Activation energy E (kJ/mole)	Activation volume Δv^* (cm^3/mole)
Dicyclohexyl peroxydicarbonate	100	107	116	4.3
Dioctanoyl peroxide	127	133	129	5.9
t-Butyl perneodecanoate	113	119	103	6.1
t-Amyl perneodecanoate	124	133	102	7.0
t-Butyl perpivalate	123	131	110	6.1
t-Amyl perpivalate	124	135	113	9.4
Di-t-butyl peroxide	191	203	152	13.4
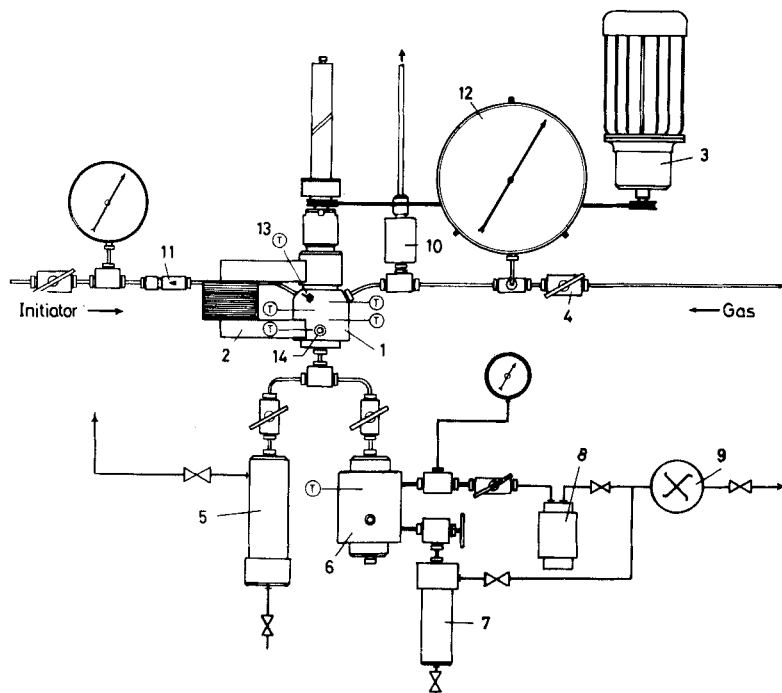
FIG. 4. Continuously operating stirred tank reactor. Maximum pressure: 3000 bar. Maximum temperature: 350°C. (1) Stirred tank reactor. (2) Heating. (3) Driver. (4) Inlet Valve. (5) Separator. (6) High-pressure separator. (7) Low-pressure separator. (8) Wax separator. (9) Flow meter. (10) Rupture disk. (11) Check valve. (12) Manometer. (13) Thermocouple. (14) Sapphire window.

temperature range because their rate of decomposition is less temperature-dependent.

Consumption and Costs

Experience has shown that the half-lives determined at high pressures and simultaneously high temperatures are a useful criterion for the preselection of a peroxidic initiator. However, further details become evident only when the effectiveness of the peroxide is examined in a polymerization test [6].

For this purpose we used a continuously operating laboratory apparatus [7], the construction and method of operation of which correspond to the flow chart of a large-scale plant illustrated earlier (Fig. 4).

The center-piece is a small stirred tank autoclave with a 15 mL capacity in which the polymerization can be carried out at pressures of up to 3000 bar and temperatures of up to 350°C. The ethylene is compressed by means of a multistage diaphragm compressor. The initiator is dissolved in a hydrocarbon and passed into the reactor through a metering device or added to the ethylene in a separate agitated vessel. After the reactor, the polymer formed is separated from the unreacted ethylene by pressure release and its amount is determined by gravimetry.

In Fig. 5 this quantity is plotted on the ordinate as the amount converted; di-octanoyl peroxide was used as initiator in this experiment. The polymerization was carried out at different temperatures from 110 to 330°C with the same initiator concentration in the ethylene introduced, the same mean residence time, and at the same pressure. As shown, the conversion increases strongly at first with rising temperatures to reach a maximum and then decreases again rather surprisingly.

The initiator consumption per kg polymer produced can be calculated from the conversion and the amount of initiator used. As shown in the diagram on the right-hand side, the initiator consumption decreases with increasing polymerization temperature, passes through a favorable application range with minimum consumption, and then increases again. The same course is obtained with all the peroxides examined; the position of the minimum differs from one peroxide to another both with respect to consumption and optimum polymerization temperature. Whereas the dioctanoyl peroxide (V) considered, and even more so t-butyl peroctoate (I), isononanoate (VIII) and t-butyl perpivalate (III) are particularly suitable for average polymerization temperatures, t-butyl peroxide (X) and t-butyl perbenzoate (IX) can be recommended for high temperature ranges (Fig. 6).

Suitable low temperature initiators are t-butyl perneodeconoate (VII) and dicyclohexyl peroxydicarbonate (VI) in particular. Allowance should be made for the fact that the most favorable range of application can alter slightly if polymerization is carried out at different pressures or with different mean residence times. Furthermore, the initiator consumption and the optimum temperature range is influenced when cyclic olefins, vinyl acetate, or styrene and its alkyl homologs are present [8]. The different prices of the peroxides should also be considered when the selection is made. There is a reluctance in scientific quarters to talk about prices; however, they often play a decisive part in practice. It needs to be mentioned here that peroxydicarbonates and other low-temperature initiators are relatively dear, because of the raw material situation, compared with di-t-butyl peroxide or t-butyl perbenzoate.

Process Control

Apart from the level of minimum consumption and the corresponding temperature, the different forms of the consumption curves should
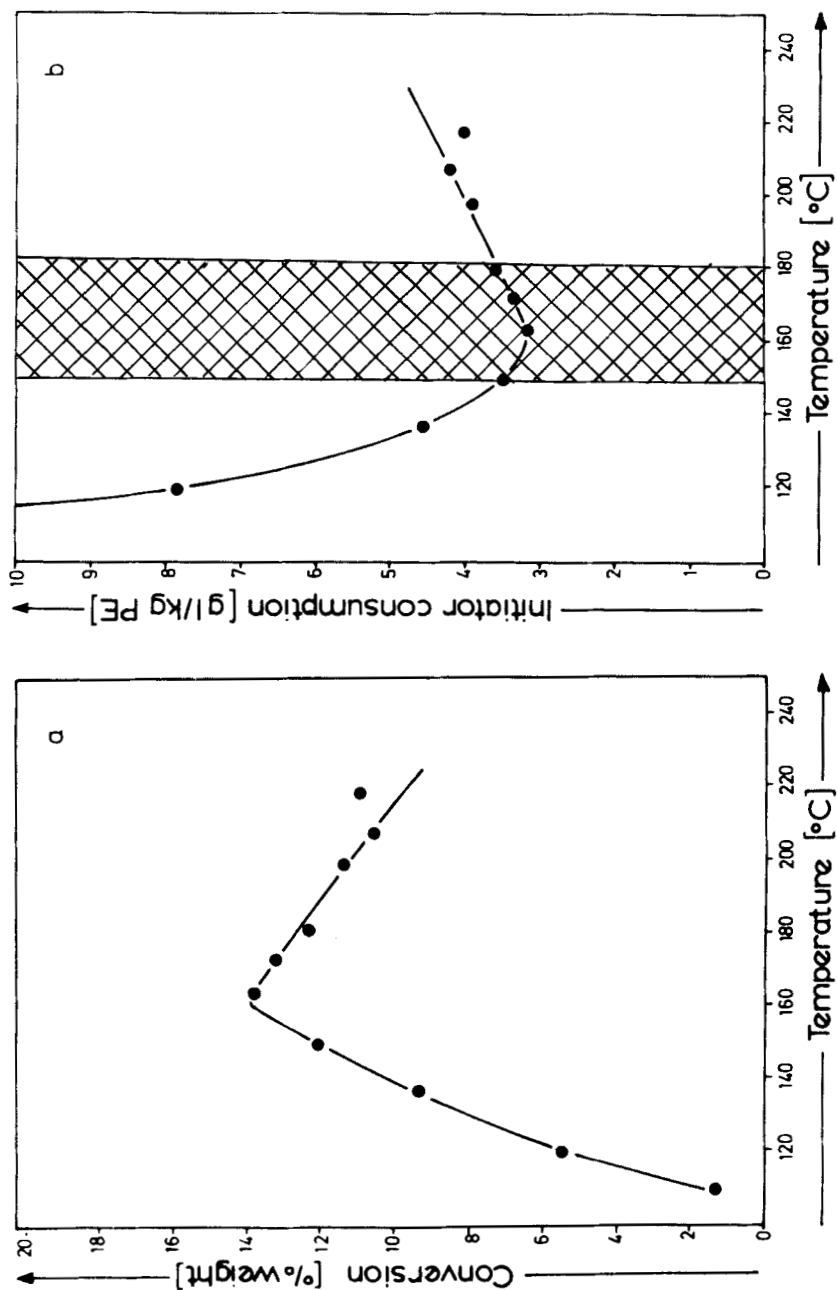
FIG. 5. Influence of the temperature on (a) conversion and (b) consumption of initiator. Initiator: dioctanoyl peroxide. Mean residence time: 65 sec. Initiator concentration in the inlet: 420 ppm. Pressure: 1700 bar.
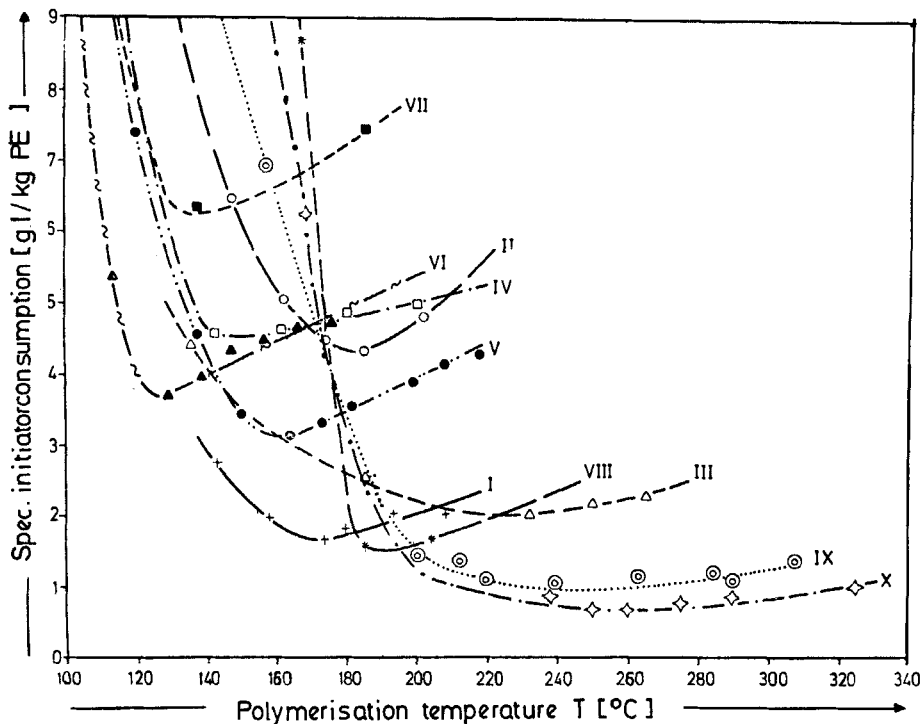
FIG. 6. Consumption of different initiators. (I) t-butyl per(2-ethyl)-hexanoate (t-butyl peroctoate); (II) diisononanoyl peroxide; (III) t-butyl perpivalate; (IV) dilauroyl peroxide; (V) dioctanoyl peroxide; (VI) dicyclohexyl percarbonate; (VII) t-butyl perneodecanoate; (VIII) t-butyl per-3,5,5-trimethylhexanoate (isononanoate); (IX) t-butyl perbenzoate; (X) di-t-butyl peroxide. Pressure: 1700 bar. Mean residence time: 65 sec. Initiator concentration: 40 ppm (molar).

be considered. Peroxides with a wide curve, such as t-butyl perpival-ate, have a constant consumption over a wide temperature range. They are therefore particularly suitable for polymerization in the tubular reactor where the temperature alters considerably along the reaction tube.

In addition, the shape of the curve affects the operating behavior of the reactor and particularly the temperature development. The wide consumption curve means a more gradual temperature increase and a much wider temperature profile in the tubular reactor, which will fluctuate less with variations in monomer input, temperature, or quantity of initiator.

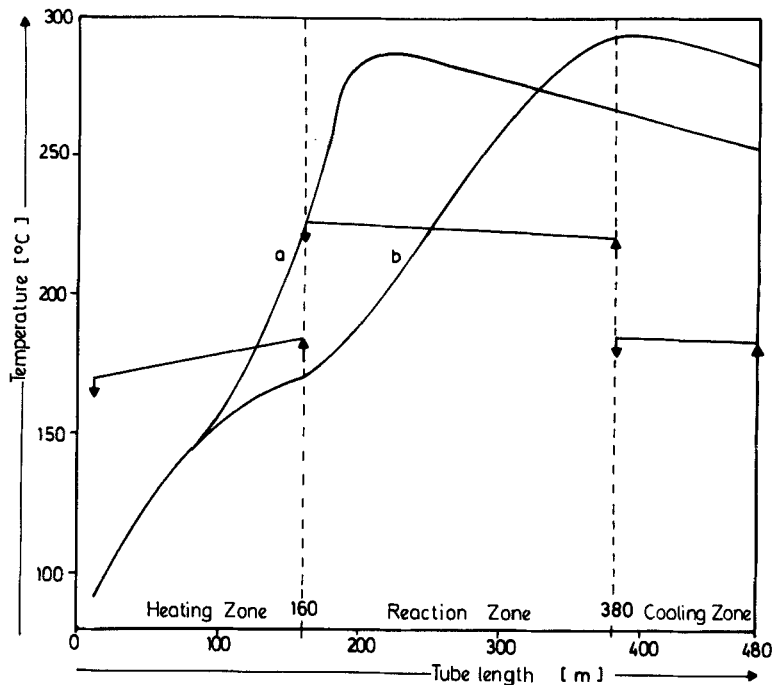In contrast, peroxides with a narrow consumption curve, i.e.,

FIG. 7. Temperature profiles in a tubular reactor. (a) Initiator with low decomposition temperature and narrow consumption curve. (b) Initiator with higher decomposition temperature and broader consumption curve.

strong dependence of consumption on temperature, cause a steep temperature increase in the tubular reactor and greater sensitivity of the reactor to changes in the operating conditions, whether deliberate or accidental.

These are the main aspects of the course of the reaction and temperature control in the polymerization reactors (Fig. 7). The temperature profile, which differs depending on the initiator, also affects the structure and the properties of the polymers formed.

EFFECT ON THE POLYMER PROPERTIES

This brings us to the second point which is of importance when selecting the initiator: the question whether the initiator influences the properties of the polymer to be made. Such an influence can be exerted by the initiator in several ways:

Indirectly via the conversion and the temperature in the reactor depending on the initiator, as mentioned above.
Directly through the reaction of the initiator or its decomposition products with the polymer or the polymer chain radicals.
By the initiator decomposition products or residual initiator which remains dissolved in the polymer.

Effect of Conversion and Temperature on the Polymer Properties

The suitability of high-pressure polyethylene for application and processing is determined mainly by the number of short-chain and long-chain branches, the mean molecular weight, and the molecular weight distribution. The initiator has an indirect effect on these values since the number of short chain branches V_K, for example, depends on the ratio of the rate of reaction of an intramolecular chain transfer $k_{tr}[R]$:

$$V_K = \frac{k_{tr}[R]}{k_{gr}[R][M]}$$

to the chain growth $k_{gr}[R][M]$. k_{tr} and k_{gr} are the rate constants of the chain transfer and the chain growth, respectively, $[R]$ is the concentration of chain radicals, and $[M]$ is the concentration of the monomer.

This ratio increases with decreasing monomer concentration, in other words, with increasing conversion and, because of the higher activation energy of the transfer reaction, with increasing temperature. The result is similar in the case of the number of long-chain branches. Since, as we have seen, different conversions are obtained with individual peroxides in identical concentrations in the monomer, and consequently different temperature developments in the reactor, short- and long-chain branched polymers of different strengths would be expected.

To investigate this possibility, we have systematically examined the products obtained from polymerization tests with different initiators. Figure 8 shows the density as a measure of the number of short-chain branches, plotted against the polymerization temperature. High densities correspond to a low degree of short chain branching and vice versa. This illustrates the well-known relationship that the density of polymers obtained under identical conditions of pressure, initiator input concentration, and residence times decreases with increasing temperature. When each peroxide is examined individually, the results confirm that the degree of conversion influences the number of short chains and hence the density.

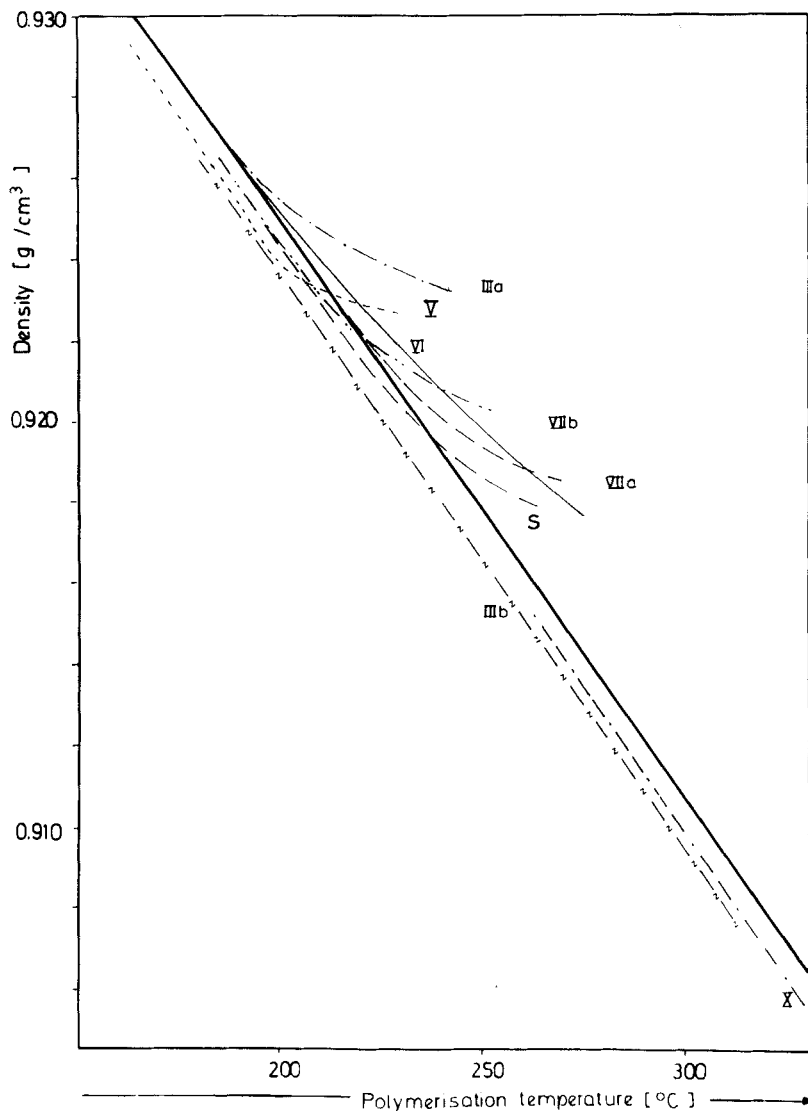FIG. 8.   Dependency of the polymer density on the synthesis tem-
perature.   Initiator (I) t-butyl-per(2-ethyl)-hexanoate; (IIIa) t-butyl
perpivalate; (IIIb) t-amyl perpivalate; (V) di-octanoyl peroxide; (VI)
di-cyclohexyl peroxidicarbonate; (VIIa) t-butyl perneodecanoate; (X)
di-t-butyl peroxide; (S) Oxygen. Pressure: 1700 bar. Mean resi-
dence time: 40 sec. Initiator concentration: 40 ppm (molar).

FIG. 9. Dependency of the mean molecular weight and the intrinsic
viscosity on the synthesis temperature. Initiator (I) t-butyl-per(2-
ethyl)-hexanoate; (IIIa, ○) t-butyl perpivalate; (IIIb,●) t-amyl per-
pivalate; (V, ＊) di-octanoyl peroxide; (VI, ▽) di-cyclohexyl peroxi-
dicarbonate; (VIIa, □) t-butyl perneodecanoate; (VIIb, ■) t-amyl
perneodecanoate; (X, △) di-tert-butyl peroxide; (S, ×) Oxygen.
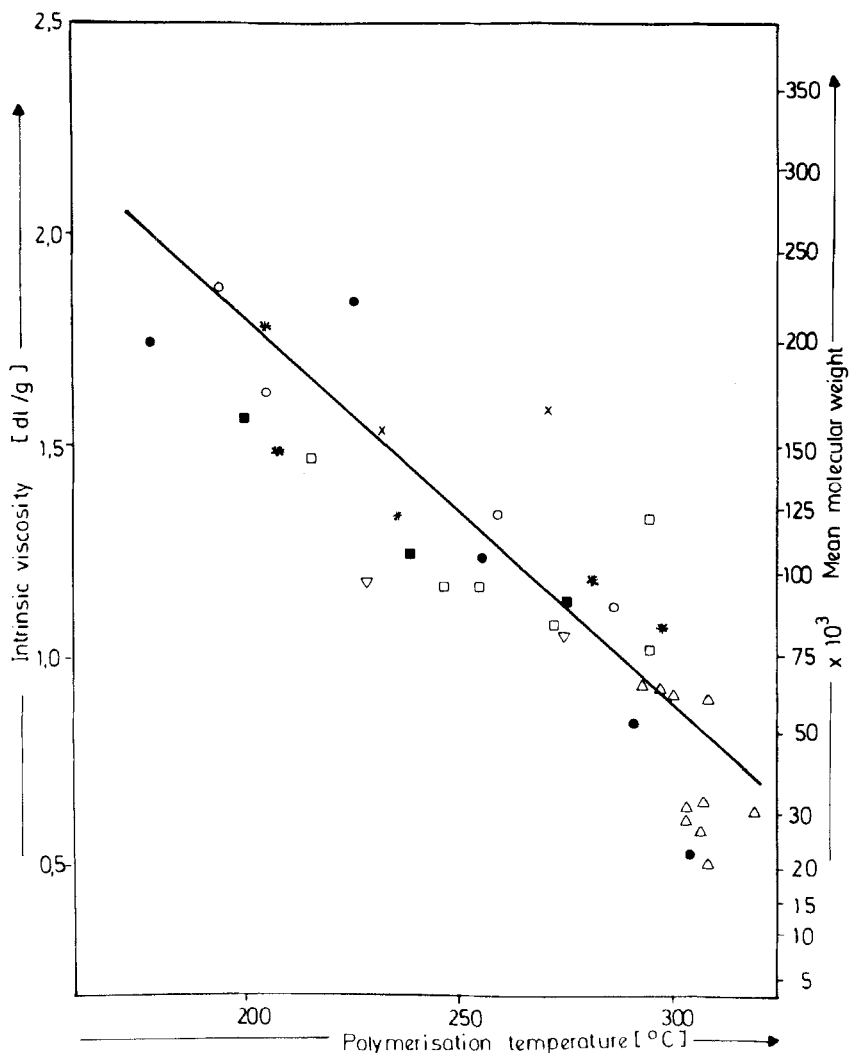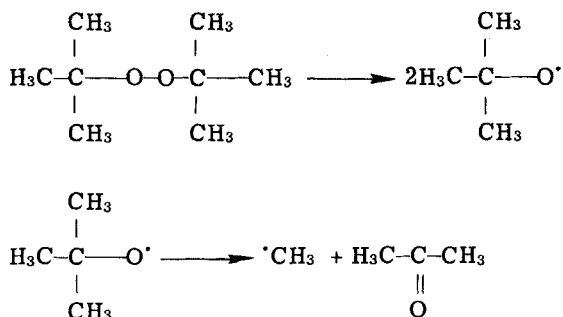Pressure: 1700 bar. Mean residence time: 40 sec. Initiator concen-
tration: 40 ppm (molar).

Polymers whose density lies below the regression curve repre-
senting all the data are the product of tests in which the initiator gave
an above average conversion. This is a clearly illustrated with di-t-
butyl peroxide (X), and t-amyl perpivalate (IIIb).

The mean molecular weight, on the other hand, is not influenced
by the initiator, as shown by Fig. 9. The polymer molecular weights
which are attributable to the individual peroxides and plotted on the
ordinate on the right-hand side have a random distribution. Only the
usual decrease in the mean molecular weight with increasing polym-
erization temperature is obtained. The same applies to the crystal-
lite melting point which is plotted against the polymerization tempera-
ture in Fig. 10.

Reaction with the Polymer

There are numerous possible ways in which the initiator decom-
position products can directly influence the polymer. For example,
additional radical sites may be formed on the polymer chain radical
or on the polymer itself as a result of hydrogen abstraction by high
energy radicals from decomposition of the initiator. These radical
sites may result in increased long-chain branching, undesirable
cross-linking, or, as a result of subsequent depolymerization, lower
molecular weights and an increased proportion of olefin groups in
the polymer. These high-energy radicals can arise by secondary
decomposition of the primary radicals formed by homolytic cleavage
of the initiator. For example, di-t-butyl peroxide, (a dialkyl per-
oxide), decomposes in one step into butyroxy radicals. These further
decompose to give a methyl radical and acetone:

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
H_3C-C-O-O-C-CH_3 \longrightarrow & 2H_3C-C-O^{\cdot} \\
| & | & | \\
CH_3 & CH_3 & CH_3
\end{array}
$$

$$
\begin{array}{c}
CH_3 \\
| \\
H_3C-C-O^{\cdot} \longrightarrow {}^{\cdot}CH_3 + H_3C-C-CH_3 \\
| \qquad\qquad\qquad\qquad || \\
CH_3 \qquad\qquad\qquad\qquad O
\end{array}
$$

In the case of diacyl peroxides, the secondary decomposition gives
2 moles of CO_2 per mole of initiator, as well as a radical. This is
illustrated by dibenzoyl peroxide
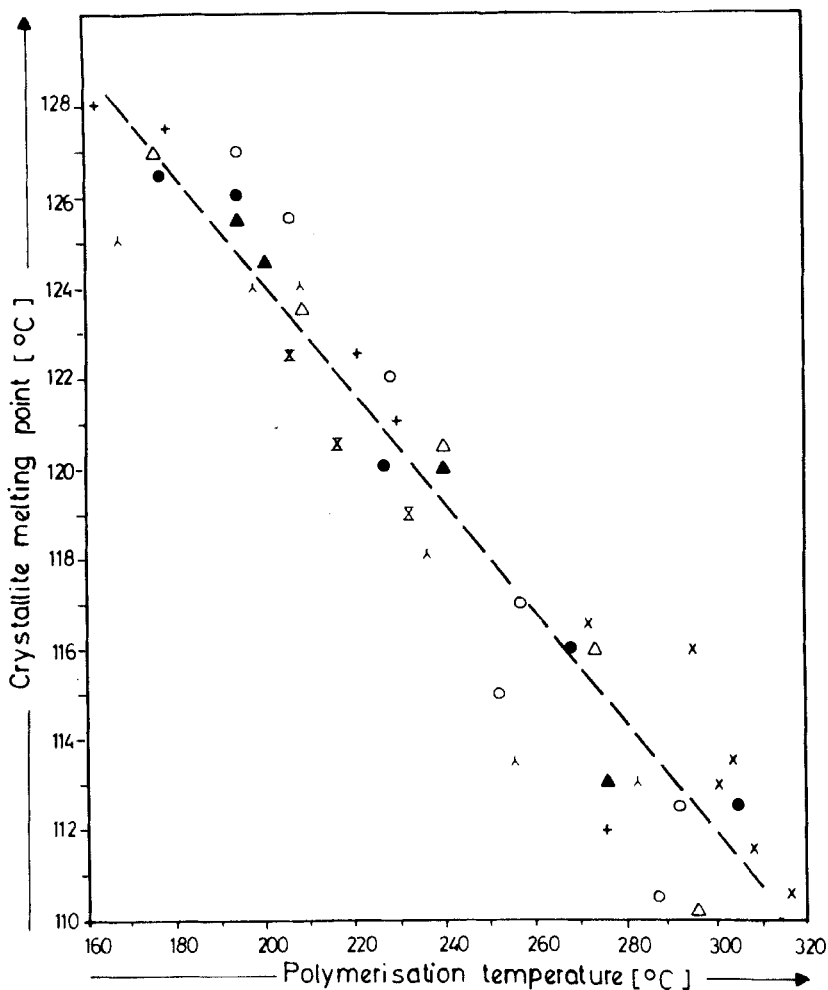
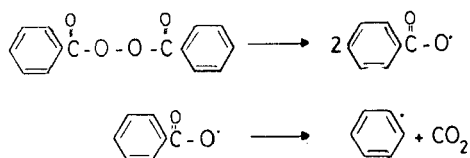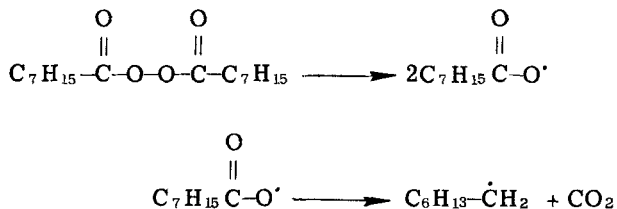FIG. 10. Dependency of the crystallite melting point on the syn-
thesis temperature. Initiator (IIIa, ○) t-butyl perpivalate; (IIIb, ●)
t-amyl perpivalate; (V, ⅄) di-octanoyl peroxide; (VI, +) di-cyclohexyl
peroxidicarbonate; (VIIa, △) t-butyl perneodecanoate; (VIIb, ▲) t-amyl
perneodecanoate; (X, ×) di-t-butyl peroxide. Pressure: 1700 bar.
Mean residence time: 40 sec. Initiator concentration: 40 ppm
(molar).

and dioctanoyl peroxide:

$$C_7H_{15}-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_7H_{15} \longrightarrow 2C_7H_{15}\overset{\overset{O}{\|}}{C}-O^{\cdot}$$

$$C_7H_{15}\overset{\overset{O}{\|}}{C}-O^{\cdot} \longrightarrow C_6H_{13}-\overset{\cdot}{C}H_2 + CO_2$$

In the same way, CO_2 formation from peroxy-dicarbonates is also possible as the decomposition of dicyclohexyl peroxydicarbonate shows:
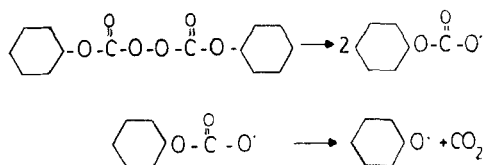
In the case of peresters, the decomposition rate is influenced to a surprising extent by the nature of the α-substituent. This cannot be explained solely by the inductive effect influencing on the O–O bond; in fact, a different decomposition mechanism occurs [9]. Since the rate of decomposition increases in parallel with the stability of the radical in the remainder, a radical fragmentation was postulated during which decarboxylation is likely to take place when the peroxide bond is split (concerted decomposition). A methyl radical can then be split off from the t-butoxy radical in a secondary reaction. This mechanism is suggested for the decomposition of t-butyl perpivalate

$$\underset{\substack{\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{O}-\text{C}-\text{C}---\text{CH}_3 \\ | \qquad\qquad | \\ \text{CH}_3 \qquad \text{CH}_3}}{\overset{\substack{\text{O CH}_3 \\ || \ | }}{}} \longrightarrow \underset{\substack{\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}---\text{O}^{\bullet} \\ | \\ \text{CH}_3}}{} + \text{CO}_2 + \underset{\substack{\text{CH}_3 \\ | \\ {}^{\bullet}\text{C}---\text{CH}_3 \\ | \\ \text{CH}_3}}{}$$

$$\underset{\substack{\text{CH}_3 \\ | \\ \text{HC}_3-\text{C}---\text{O}^{\bullet} \\ | \\ \text{CH}_3}}{} \longrightarrow {}^{\bullet}\text{CH}_3 + \underset{\substack{|| \\ \text{O}}}{\text{H}_3\text{C}-\text{C}-\text{CH}_3}$$
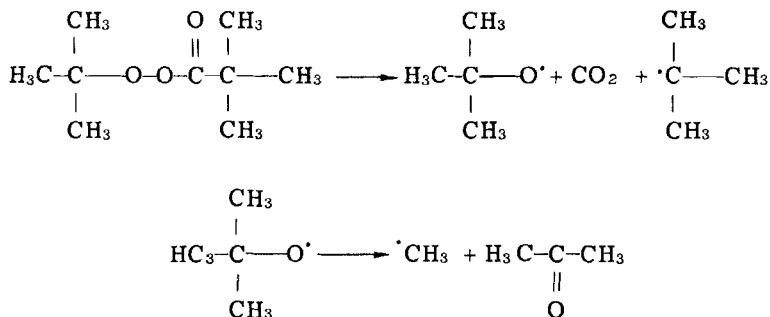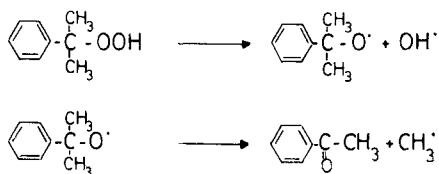
and for t-butyl perbenzoate:
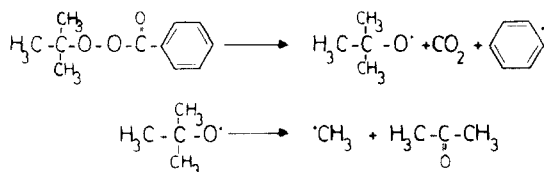
The different reactivities of the radicals formed during the decomposition of the individual peroxides would suggest, in line with the details provided above, that polymers produced under identical conditions should have different degrees of long-chain branching or cross-linking, and consequently different flow properties and different optical properties. The investigations carried out so far into this problem do not allow a definite answer to be given.
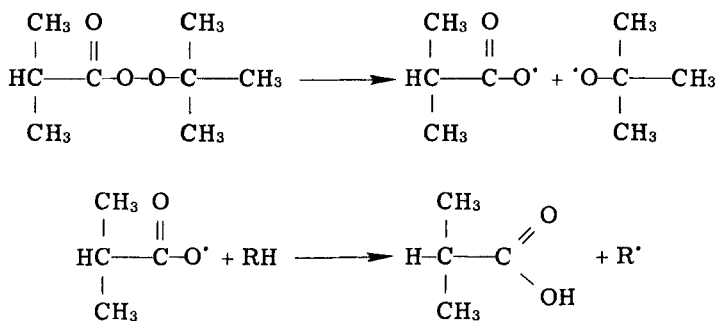
It is reported that with polymerization in industrial tubular reactors the optical properties of films deteriorate and undesirable extrusion expansion is increased by elastic recovery of the extruded material when peroxides having a short half-life are mixed with the cold gas which is added upstream in order to increase conversion [10]. Also, trials in industrial scale autoclave reactors have shown effects of the peroxide on the flow properties and the optical properties of the polymer produced.

Initiator Decomposition Products

The position is quite clear when substances which have a strong odor or are toxic are formed during initiator decomposition. An example is cumene hydroperoxide, the secondary decomposition of which gives acetophenone as well as a methyl radical:

$$C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OOH \longrightarrow C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O^{\bullet} + OH^{\bullet}$$

$$C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O^{\bullet} \longrightarrow C_6H_5-\underset{\underset{\displaystyle O}{||}}{C}-CH_3 + CH_3^{\bullet}$$

Such peroxides cannot therefore be employed for the production of polymers which are used as packaging or coating materials in the food sector. The odoriferous substances need not be direct decomposition products of peroxide but may be formed by the reaction of decomposition products with the solvent or with polymerization additives such as molecular weight modifiers and with comonomers. In this way, i-butyric acid, which has an unpleasant odor, can be formed through hydrogen abstraction at the solvent by a primary radical of t-butyl perisobutyrate:

$$\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{HC}}-\underset{\underset{\displaystyle}{}}{\overset{\overset{\displaystyle O}{||}}{C}}-O-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{HC}}-\underset{}{\overset{\overset{\displaystyle O}{||}}{C}}-O^{\bullet} + {}^{\bullet}O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

$$\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{HC}}-\overset{\overset{\displaystyle O}{||}}{C}-O^{\bullet} + RH \longrightarrow \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{H-C}}-C\overset{\diagup O}{\diagdown OH} + R^{\bullet}$$

A strong inherent odor of the peroxide itself also limits its application, not because it affects the quality of the product, but because of its effect on the environment during handling. This is true of t-butyl perisobutyrate mentioned above and t-butyl peracetate. These are both initiators which, because of their effectiveness, would be suitable for polymerization temperatures of 170 to 220°C.

HANDLING OF PEROXIDES

The main considerations in the handling of peroxides during metering in and storage are questions of process technology and safety techniques.

Metering In

For metering in, the peroxidic initiators for high-pressure polymerization are dissolved in hydrocarbons, if they are solid substances, or diluted with hydrocarbons. Benzene fractions, n- and iso-dodecane, or mixtures of n-heptane and toluene are used as hydrocarbons. At the relatively low temperatures which are necessary to prevent a premature decomposition of the polymerization initiators, and with high pressure, there is the risk that the initiator will crystallize out from a concentrated solution. The crystals deposit at unsuitable locations in the metering system, e.g., in the pump valves, putting these out of action; in other words, the solution must not be too concentrated. On the other hand, it should be diluted only as far as is absolutely necessary to avoid introducing an excessive charge of solvent into the reactor and to keep investments in the metering unit and energy costs for conveying the solvent as low as possible.

In order to clarify the question as to the pressures and temperatures at which crystallization takes place and what degree of dilution is necessary to prevent it, solubility tests have been carried out [11].

For the experiments an optical high-pressure cell (Fig. 11) designed for pressures of up to 3000 bar and temperatures of -40°C was used. The measuring cell, equipped with a cooling or heating jacket, has a volume of 5 mL and is equipped with two sapphire windows, 5 mm diameter, to observe the crystallization process. The temperature in the compression chamber can be measured by a rapidly responding jacket thermocouple.

In solubility investigations the cell is filled with the peroxide solution and maintained at constant temperature using a cryostat. The internal pressure is increased in stages by means of a hydraulic pump, keeping the temperature constant and maintaining the pressure at each stage for approximately 30 min to allow the system to reach equilibrium. Pressure is increased until crystallization becomes visible through the illuminated windows and is then reduced until all the crystals redissolve. The two pressures at which crystals are observed and at which they redissolve are both recorded.

The pressure and temperature values recorded for the solubility limits are illustrated in Fig. 12 for undiluted t-butyl perbenzoate, a liquid perester which was shown earlier to be a suitable initiator for moderately high polymerization temperatures. This figure shows the same result as in crystallization at normal pressure, namely a metastable range through which the peroxide passes without crystallizing out when the pressure in increased at a constant temperature or when cooled at a constant pressure. This may be compared with supersaturation: only when a certain pressure is exceeded do crystals begin to form (supersolubility curve) which redissolve only at lower pressures (solubility curve).

The solubility increases with temperature; at elevated temperatures, higher pressures can be applied before crystallization occurs.
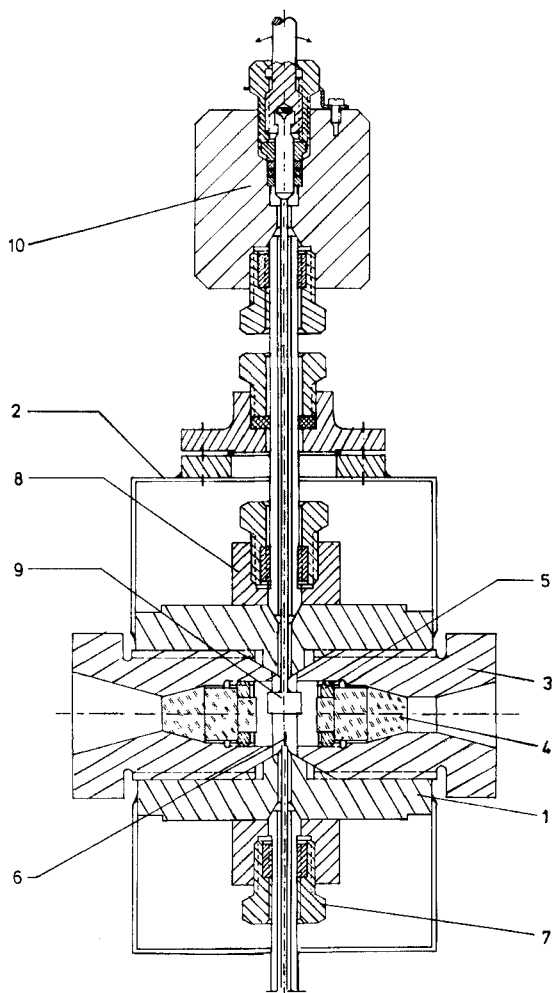
FIG. 11. Optical high-pressure cell. Maximum pressure: 3000 bar. (1) Pressure jacket. (2) Heating jacket. (3) Screw joint. (4) Sapphire window. (5) Pressure cap. (6) Thermocouple. (7) Connecting screw. (8) Pressure ring. (9) Stirrer. (10) Stirrer sealing.

Whereas crystallization takes place at normal pressure if the temperature is below 0°C, a solution heated to 30°C has a crystallization limit at pressures of 700 bar or more. Obviously this is not sufficient if the initiator is to be used at pressures of 1000 to 3500 bar as in high-pressure polymerization. The initiator must therefore be diluted
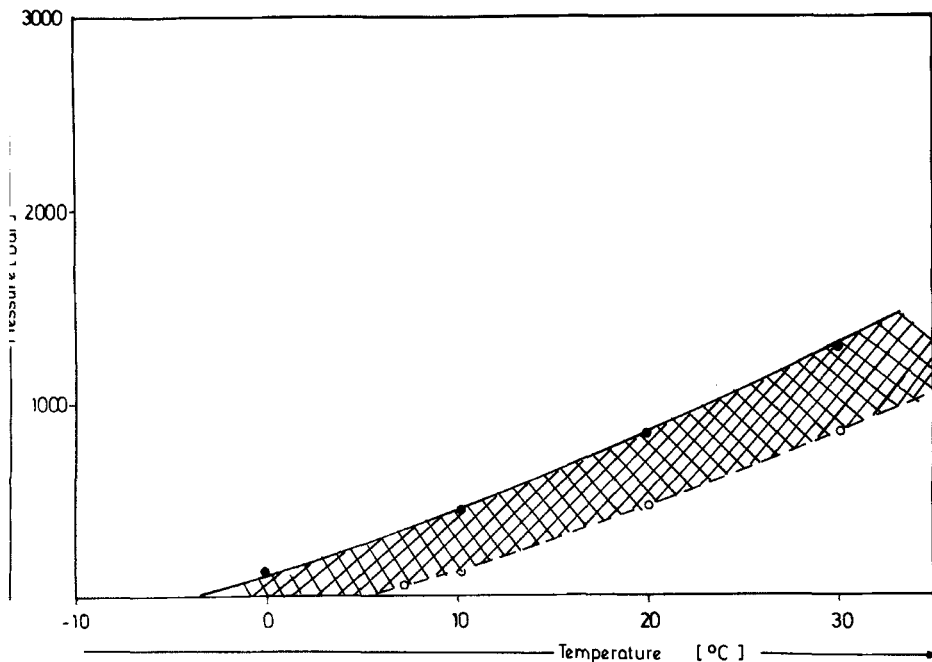
FIG. 12. Crystallization of t-butyl perbenzoate. (—) Crystalliza-
tion. (- -) Redissolvation.

to eliminate the risk of crystallization taking place under these ex-
treme conditions (Fig. 13).

A pressure of ~ 1200 bar is reached with a 50% solution by weight
of t-butyl perbenzoate in i-dodecane at 30°C. The initiator solution
needs to be diluted further for use at higher polymerization pressures.
This is unsatisfactory because the pressure of fairly large quantities
of solvent needs to be increased and, above all, because these large
quantities of solvent pass into the reactor.

We have therefore tried to find substitutes for peroxides which tend
to crystallize, e.g., t-butyl perbenzoate. This is true of a number of
peroxides which are otherwise excellent polymerization initiators but
can be used only in highly dilute form, such as the dicyclohexyl per-
oxydicarbonate mentioned above, dilauryl peroxide, decanoyl and
octanoyl peroxide, t-butyl perpivalate, or di-t-butyl peroxide. A mar-
ginal condition is that the rate of decomposition and the half-life
should be the same, and the consumption as low as possible; these
conditions cannot always be quite fulfilled. t-Butyl perneodecanoate,
for example, which has a higher solubility, has a slightly higher half-
life than the dicyclohexyl peroxydicarbonate which may be used in-
stead of dilauroyl peroxide, and decomposes slightly more slowly.
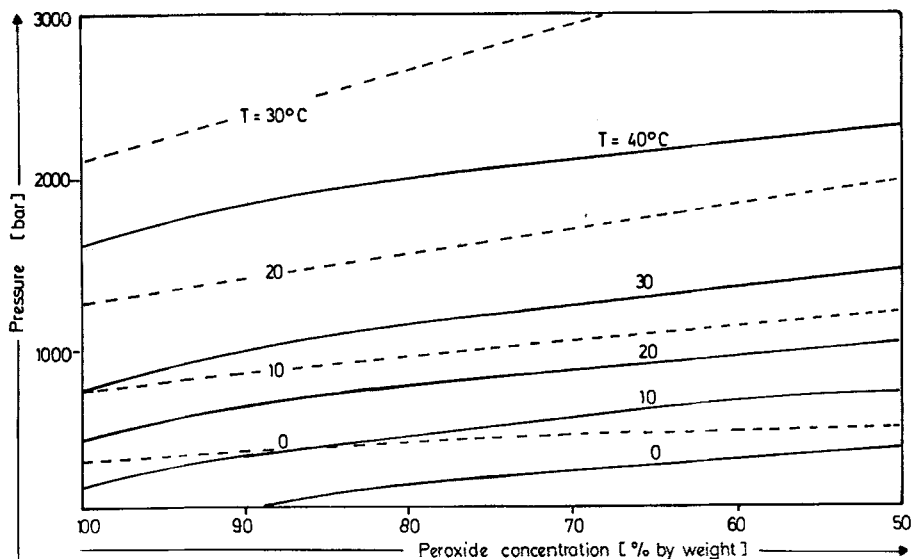When searching for peroxide substitutes with a low crystallization

FIG. 13. Solubility of t-butyl perbenzoate and t-amyl perbenzoate.
Solvent: iso-dodecane. (——) t-butyl perbenzoate. (- -) t-amyl per-
benzoate.

tendency, we have found that the solubility increases rapidly with
only a slight change in the decomposition half-life if a t-amyl group
instead of a t-butyl group is introduced in a perester. A comparison
of t-butyl and t-amyl perbenzoate clearly illustrates the reduced
crystallization tendency (Fig. 13).

Whereas pure t-butyl perbenzoate can crystallize out at 30°C at
a pressure below 700 bar, the corresponding value for the amyl
compound is considerably higher at 2100 bar. In other words, t-amyl
perbenzoate can be introduced into the reactor in the high concentra-
tion required.

Storage

Finally, both the safety and economic aspects of the storage of
peroxides must be considered. At the beginning it was mentioned that
peroxides must be stored at low temperatures in order to prevent
premature decomposition. If the critical temperature limit is ex-
ceeded, a peroxide will decompose spontaneously, the decomposition

TABLE 3. Storage of Peroxides

Trade name Chemical name Grade supplied	Structural formula	Molecular weight	Storage temperature (°C)
Peroxydicarbonates Diisopropyl peroxydicarbonate 40% solution in phthalate	CH_3—CH(CH_3)—O—C(=O)—O—O—C(=O)—O—CH(CH_3)—CH_3	206.2	~ -15
Di-n-butyl peroxydicarbonate 25% solution in aliphatics	CH_3–(CH_2)$_3$–O–C(=O)–O–O–C(=O)–O–(CH_2)$_3$–CH_3	234.3	Below -5
Dicyclohexyl peroxydicarbonate Technical pure grade, powder	H(C$_6$H$_{10}$)—O—C(=O)—O—O—C(=O)—O—(C$_6$H$_{10}$)H	286.3	Below +10
Diacyl peroxides Diisononanoyl peroxide 75% solution in aliphatics	(CH_3)$_3$C—CH_2—CH(CH_3)—CH_2—C(=O)—O—O—C(=O)—CH_2—CH(CH_3)—CH_2—C(CH_3)$_3$	314.5	-20 to ±0
Dioctanoyl peroxide Technical pure grade, flakes	CH_3–(CH_2)$_6$–C(=O)–O–O–C(=O)–(CH_2)$_6$–CH_3	286.4	Below +10
Didecanoyl peroxide Technical pure grade, flakes	CH_3–(CH_2)$_8$–C(=O)–O–O–C(=O)–(CH_2)$_8$–CH_3	342.6	Below +25

|	Structure	M.W.	Temp.
Dilauroyl peroxide Technical pure grade, flakes	$CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-CH_3$	398.6	Below +30
Peresters t-Amyl-perneodecanoate 75% solution in aliphatics	$\begin{array}{c}CH_3\\ \| \\ CH-O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-CH \\ \| \\ CH_3 \\ \| \\ CH_3\end{array}$	206.2	Below -5
t-Butyl-perneodecanoate 75% solution in aliphatics	$CH_3-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-CH_3$	234.3	Below -5
t-Butyl perpivalate 75% solution in aliphatics		286.3	Below +5
t-Butyl-per-2-ethyl hexanoate Technical pure grade, liquid	$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\|}{\underset{\|}{C}}}}-CH_2-CH-CH_2-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_2-CH-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{\|}{\underset{\|}{C}}}}-CH_3 \quad (CH_3)$	314.5	Below +20
t-Butyl-perbenzoate Technical pure grade, liquid		286.4	+10 to +30
Dialkyl peroxides di-t-butyl peroxide Technical pure grade, liquid	$CH_3-(CH_2)_6-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-CH_3$	342.6	Below +30
	$CH_3-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-CH_3$		
Alkyl Hydroperoxides t-Butyl hydroperoxide 80%, liquid	$CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-CH_3$	398.6	Below +30
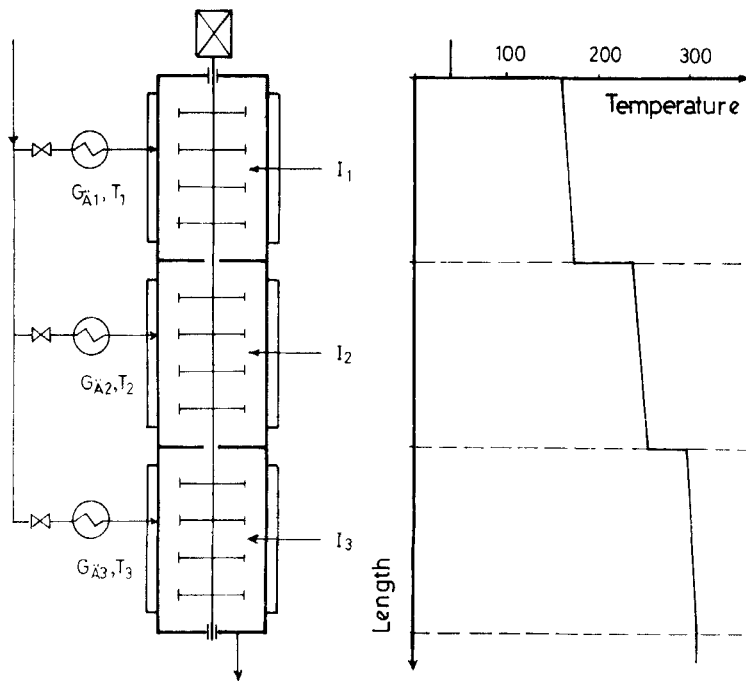
FIG. 14. Multichamber stirred tank reactor.

Chamber	Ethylene G_A (ton/hr)	Polyethylene G_P (ton/hr)	Initiator I
1	18	2.1	di-t-butyl perneodecanoate, 10 kg/hr
2	8	2	t-butyl perbenzoate, 1.4 kg/hr
3	4	1.1	di-t-butyl peroxide, 0.5 kg/hr

being accelerated by the liberated heat of reaction. The self-accelerating decomposition temperature (SADT) depends on the tendency of the peroxide to decompose, which is related to the rate of decomposition, ·the activation energy, and the heat build-up which is determined by the quantity of peroxide and its dilution. The SADT values are 50 to 60°C for stable peroxides and 20°C or less for unstable products. The storage temperature must be considerably below these values [12].

A few such values are shown in Table 3. Stable peroxides such as di-t-butyl peroxide and t-butyl perbenzoate, which can be stored at temperatures of +10 to 30°C, cause no problems. As a rule, low temperature initiators require storage temperatures of about 0 to -20°C.

It should be noted that the decomposition can be accelerated by a number of substances which act as catalysts or react with the peroxide to form radicals. These include above all the heavy metal compounds of Co, V, Fe, Mn, and Cu which have a particular effect on alkyl peroxides and hydroperoxides and peresters, whereas t-amines catalyze the decomposition of di-acylperoxides [13].

PRACTICAL EXAMPLES

Finally, the criteria discussed in respect to the choice of peroxidic initiators for high-pressure polymerization should be applied to two concrete examples.

A polyethylene with a melt flow index of 0.3 and a density of 0.921 g/cm³ for the production of heavy films can be produced in a triple chamber stirred autoclave at a pressure of 1500 to 2000 bar and the temperature stages indicated in Fig. 14.

In consideration of all the factors such as polymerization initiation, the polymer properties, and the amount of initiator, it can be recommended to use t-butyl perneodecanoate in the first chamber, t-amyl perbenzoate or t-butyl peroctoate in the second, and di-t-butyl peroxide in the last chamber. The rate of decomposition of these initiators is appropriate for the polymerization temperatures, so that low consumption can be expected. No unpleasant decomposition products are formed which would limit the application of the polymer product as a packaging material. By further processing, films with a low haze and a high gloss are obtained. The low crystallization tendency makes it possible to use relatively highly concentrated solutions. The flow rates indicated relate to a reactor with a capacity of 0.5 m³, in which an average of 5 t polyethylene can be produced hourly, namely 2 t/hr each in the two first chambers and 1 t/hr in the last chamber.

In the second example of polymerization in a tubular reactor (Fig. 15), the economy of the process is improved by multiple injection of cold ethylene. In order to initiate the reaction at low temperatures, oxygen, which is satisfactory in many processes, is often abandoned and peroxidic low temperature initiators are used. t-Butyl perneodecanoate or dicyclohexyl peroxydicarbonate (in spite of its higher price and increased crystallization tendency) are suitable since they decompose sufficiently rapidly at low temperatures. t-Butyl perpivalate and t-amyl perpivalate are suitable for multiple introduction into the reactor because they are distinguished by low consumption over a wide temperature range as it occurs in the tube reactor. As relatively high temperatures of up to 330°C arise in the
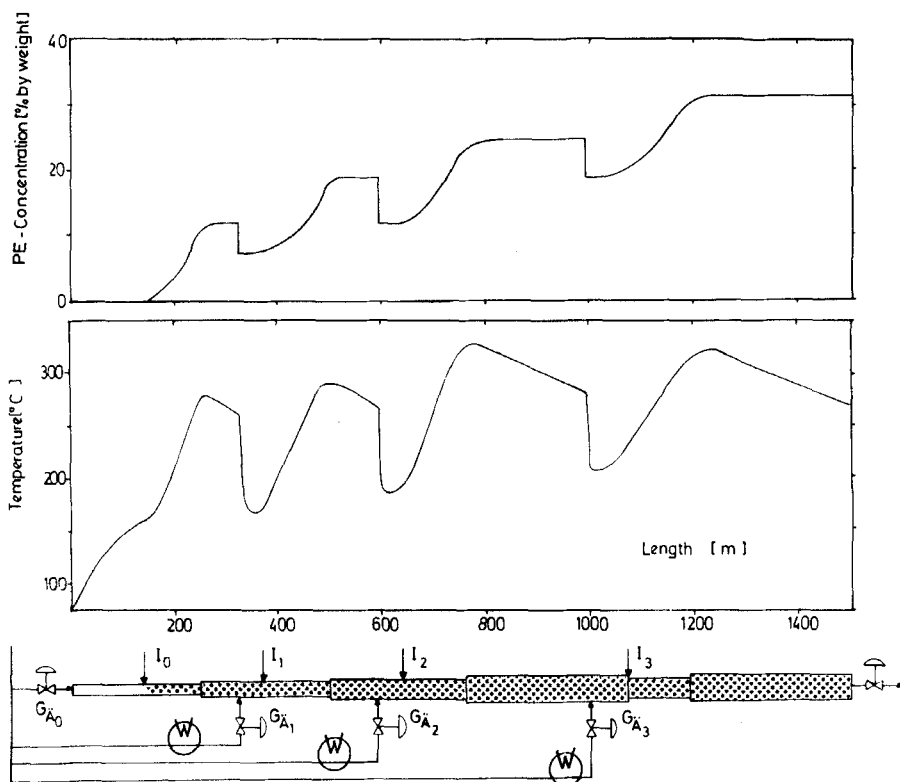
FIG. 15. Tubular reactor with multiple feed.

	Heating section	1st feed	2nd feed	3rd feed
Amounts, ton/hr	$G_{A_0} = 12.5$	$G_{A_1} = 7.8$	$G_{A_2} = 12.0$	$G_{A_3} = 13.6$
Initiator	I_0	I_1	I_2	I_3
Pressure, bar	3150	3020	2910	2750

tube reactor, peroxides with a high decomposition half-life, such as t-butyl perbenzoate, or even more stable compounds such as di-t-butyl peroxide, are added. High rates of conversion (30% and more) and consequently a high level of profitability can be achieved with these initiator combinations without adversely affecting the application and processing characteristics of the polymers.

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