Asymmetrical Bifunctional Organic Peroxides as Initiators for the High-Pressure Polymerization of Ethylene

Gerhard Luft[a]; Max Dorn[b]

[a] Institut für Chemische Technologie Technical University of Darmstadt, Darmstadt, Germany [b] Peroxidchemie Höllriegelskreuth/München, Munich, Germany

PLEASE SCROLL DOWN FOR ARTICLE

ASYMMETRICAL BIFUNCTIONAL ORGANIC PEROXIDES AS INITIATORS FOR THE HIGH–PRESSURE POLYMERIZATION OF ETHYLENE

GERHARD LUFT

Institut für Chemische Technologie
Technical University of Darmstadt
Darmstadt, Germany

MAX DORN

Peroxidchemie
Höllriegelskreuth/München
Munich, Germany

ABSTRACT

As a follow-up to earlier investigations into the high-pressure polymeri-
zation of ethylene with symmetrically substituted bifunctional peroxides,
the suitability of 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate, a
peroxide with different substituents on both O—O groups, has been
tested. The polymerization tests were carried out in continuous opera-
tion in a stirred autoclave at 1700 bar, 240-285°C, a residence time of
60 s, and an initiator concentration of 3-25 mol ppm in the feed. Con-
versions of up to 30% were achieved. The specific initiator consump-
tion was 0.2-1 g initiator per kg polyethylene. The density of the poly-
mers obtained was 0.915-0.925 g/mL, their average molecular weight
was 40×10^3 to 60×10^3, and their melt flow index was 0.001-100
g/10 min. On the basis of the molecular weight distribution, polydis-
persities of 4-7 were obtained.

INTRODUCTION

In the course of a previous investigation [1], the suitability of bifunctional organic peroxides for the high-pressure polymerization of ethylene was investigated. The peroxides chosen for this investigation, namely 2,5-dimethyl-hexane-2,5-bis perpivalate (Peroxide II), 2,2-bis(t-butylperoxy)butane (III), and 2,5-dimethylhexane-2,5-di-t-butyl peroxide (IV), were symmetrical compounds of the type
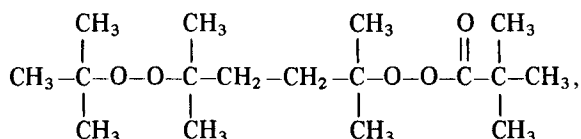
$$R_1-O-O-R_2-O-O-R_3,$$
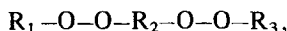
with the same substituents R_1 and R_3 on both O–O groups.

In the course of polymerization tests it was found that, from the molar point of view, only half the amount of a bifunctional initiator needs to be metered into the ethylene feed compared to a corresponding monofunctional peroxide. This led to the conclusion that twice as many radicals are formed during the decomposition of bifunctional peroxides. Depending on the pressure and temperature, the decomposition can preferably take place as a stepwise or as a concerted reaction, as shown by separate decomposition measurements [2]. The likelihood of the cleavage of the two O–O bonds taking place is the same because of the symmetrical structure of the above-mentioned peroxides. The situation changes when the substituents R_1 and R_3 differ from each other.

In order to investigate whether this influences the polymerization reaction and the products obtained, polymerization tests were carried out with an asymmetrically substituted bifunctional peroxide.

MATERIALS AND EXPERIMENTS

The asymmetrically substituted peroxide selected was 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate (Peroxide I),

$$
\begin{array}{ccccc}
CH_3 & CH_3 & & CH_3 & O\ CH_3 \\
| & | & & | & \|\ | \\
CH_3-C-O-O-C-CH_2-CH_2-C-O-O-C-C-CH_3, \\
| & | & & | & | \\
CH_3 & CH_3 & & CH_3 & CH_3
\end{array}
$$

which was specially synthesized for these investigations. Its molecular weight is 318, and its active oxygen content 10.1%, based on the pure peroxide.

The ethylene used had the following specifications: ethylene, >99.95 vol%; ethane, <150 vol ppm; methane, <120 vol ppm; other hydrocarbons, <100 vol ppm; oxygen, <5 vol ppm; nitrogen, <50 vol ppm; and water, <30 vol ppm.

Before the polymerization reaction, the ethylene was passed over a copper-containing catalyst (BASF R3-11) to remove the residual oxygen.

The polymerization tests were carried out in continuous operation in a stirred autoclave. The pressure was 1700 bar, the residence time 60 s. The initiator was metered into the feed gas in the form of a 30 wt% solution in *n*-octane. The concentration in the feed gas was varied between 3 and 25 mol ppm. Under these conditions, temperatures of 240-285°C were reached in the reactor. The temperature level in the polymerization reactor could be influenced, at a given initiator concentration, by the input temperature of the feed gas.

The polymer was isolated on leaving the reactor by releasing the pressure, and its quantity was determined gravimetrically. To determine the characteristics of the polymer, the density, the average molecular weight, the molecular weight distribution, and the melt flow index were determined.

RESULTS

The quantity of polymer formed and the amount of ethylene supplied were used to determine the conversion, which is plotted in Fig. 1. With rising temperatures, there is an almost linear increase in conversion which levels off after a maximum has been reached. As expected, the conversion also increases with increasing initiator concentration in the feed, the increase being substantial initially and then leveling off with a high initiator concentration. With a rising initiator concentration, the maximum conversion moves toward higher temperatures. Overall levels of conversion of up to 30% were achieved.

The initiator consumption was R (in g initiator per kg polyethylene) calculated from the conversion x (%) and the initiator concentration ($I°$) (mol ppm) in the feed according to

$$R = 0.1 \frac{[I°] \, M_I}{x \, M_E},$$

(1)

where M_I is the molecular weight of the initiator and M_E that of ethylene. With a high initiator concentration of 25 mol ppm in the feed, a high initiator consumption of 1 g I/kg PE was obtained. With a low initiator concentration
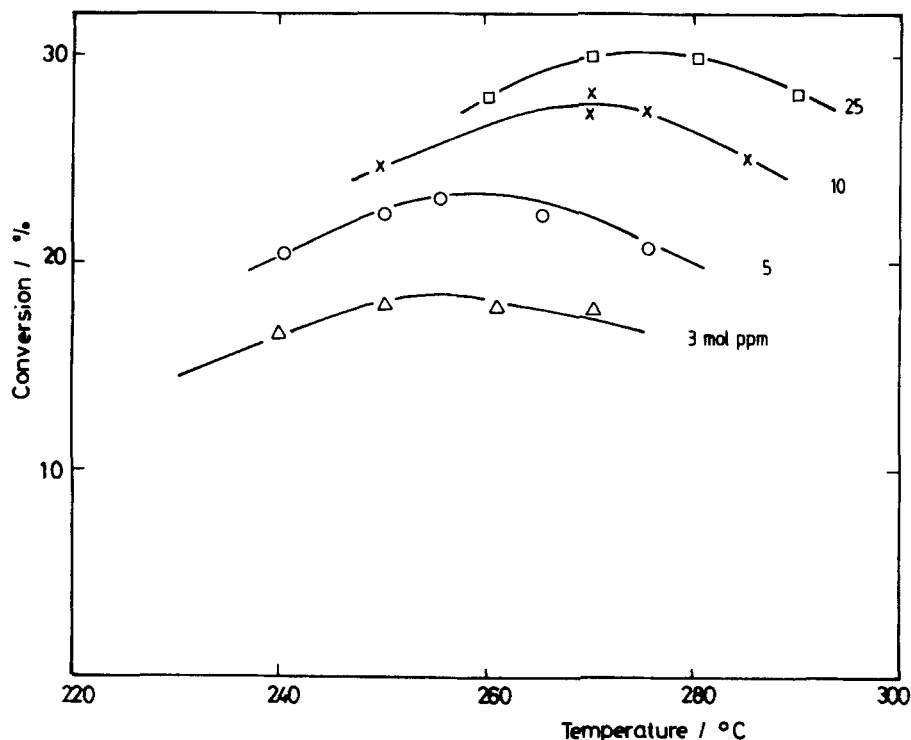
FIG. 1. Conversion. Pressure, 1700 bar; residence time, 60 s.

of 3 mol ppm, on the other hand, only 0.2 g was required to produce 1 kg PE. The initiator consumption/temperature curves present a flat minimum which moves toward higher temperatures with rising initiator concentrations (Fig. 2).

The polymer density determined at 20°C according to the suspension method in an isopropanol/water mixture is plotted in Fig. 3 against the polymerization temperature. Under the polymerization conditions chosen, polymers with a density of between 0.915 and 0.925 g/mL were obtained. When the temperature in the polymerization reactor is raised by 10°C, the density of the polymers produced decreases by 0.0025 g/mL. At a given polymerization temperature, the initiator concentration in the feed gas has practically no effect on the density.

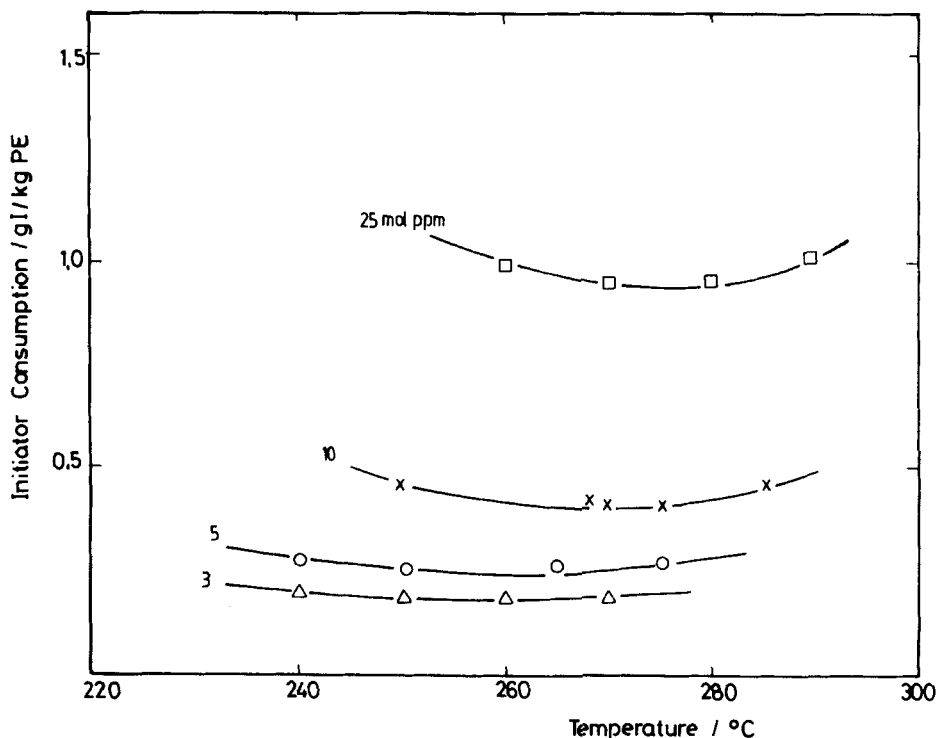The molecular weight distribution of the polymers was determined by gel

FIG. 2. Initiator consumption. Pressure, 1700 bar; residence time, 60 s.

permeation chromatography. Three Styragel columns (pore diameter 500-
10^6 Å, particle size 10 μm) connected in series and a preliminary column
(pore diameter 50 Å) were used. The measurements were carried out at
145°C. Trichlorobenzene was the solvent used. Two typical molecular
weight distribution curves are shown in Fig. 4. The broad, bimodal molecu-
lar weight distribution curves are representative of all the specimens obtained
with this particular bifunctional peroxide initiator.

The average molecular weights were calculated from the distribution curves
(see Fig. 5). Both MW averages decrease in the same way with increasing ini-
tiator concentration in the feed.

The polydispersities were 7-10 for the different polyethylenes obtained at
identical pressure and temperature but with different initiator concentrations.
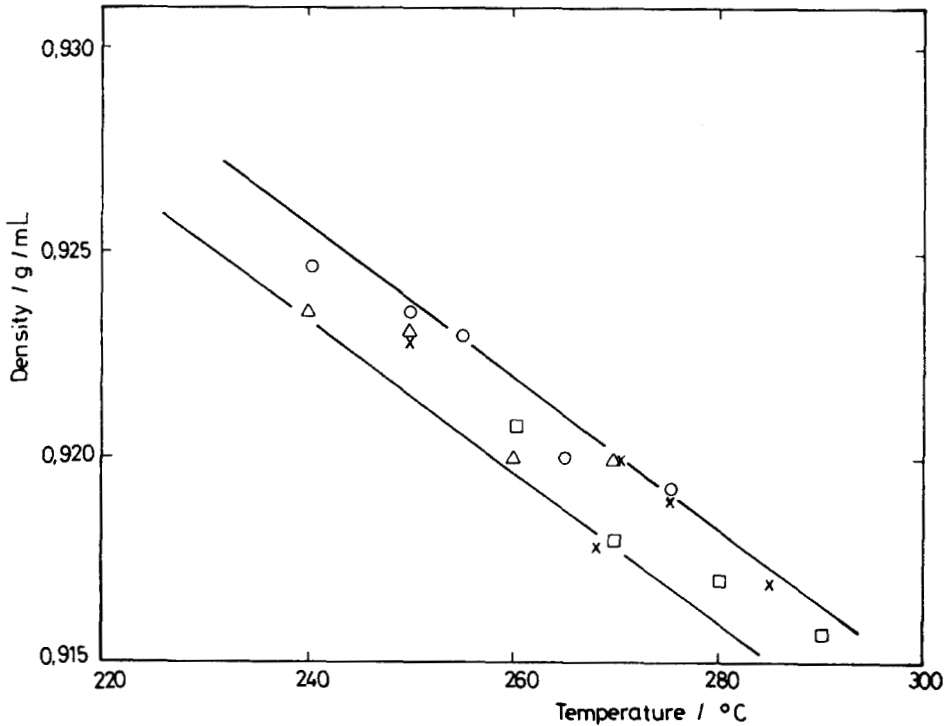
FIG. 3. Density. Pressure, 1700 bar; residence time, 60 s; (□) 25 mol ppm, (X) 10 mol ppm, (○) 5 mol ppm, (△) 3 mol ppm.

The melt flow index (*MI*) at 190°C with 2.16 kg was 0.1-2.8 g/10 min. For higher values, the temperature was reduced to 125°C while values below 0.1 g/10 min were determined at 190°C with 21.6 kg and converted, like the values measured at 125°C, to 190°C and 2.16 kg as follows:

$$MI_{190°, \, 2.16} = 2.9636 + 1.6667 \times 10 \, g \, MI_{190°, \, 21.6},$$

$$MI_{190°, \, 2.16} = 0.9394 + 0.9174 \times 10 \, g \, MI_{125°, \, 2.16}.$$

The melt flow index varies inversely with the average molecular weight. As shown in Fig. 6, the melt flow index increases semilogarithmically with the polymerization temperature. An increase in the initiator concentration in the
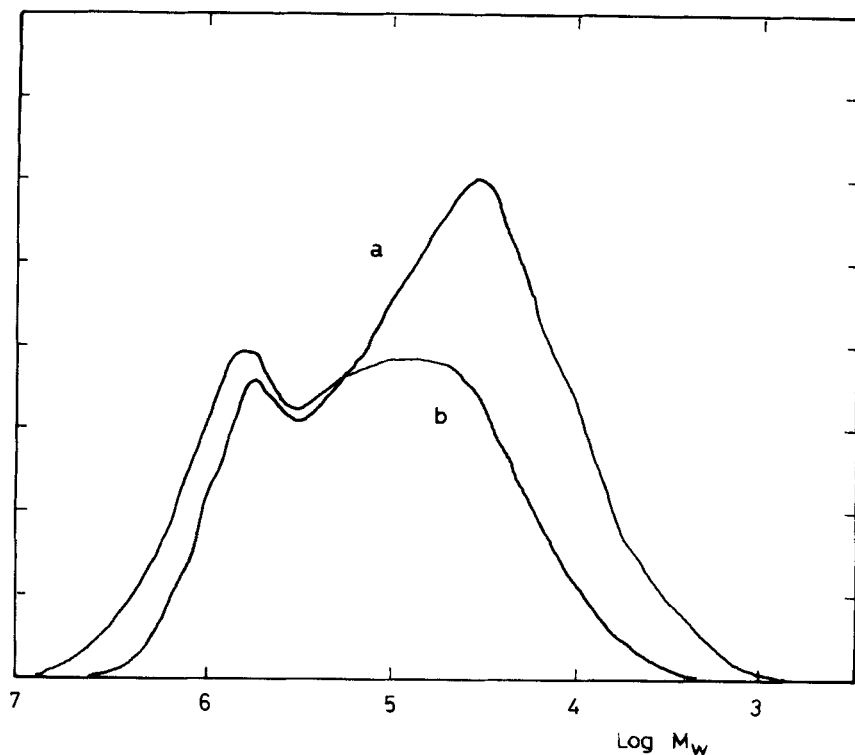
FIG. 4. Molecular weight distribution. Curve a: Pressure, 1700 bar; temperature, 285°C; initiator concentration, 10 mol ppm; residence time, 60 s. Curve b: Pressure, 1700 bar; temperature, 240°C; initiator concentration, 3 mol ppm; residence time, 60 s.

feed from 5 to 25 mol ppm, the polymerization temperature being constant, causes, on the average, a tenfold increase in the melt index of the polyethylene produced.

To determine the long-chain branching frequency, the intrinsic viscosity in trichlorobenzene was measured also at 145°C. The long-chain branching frequency of the polymer specimens selected (Fig. 7), as expected, increases strongly with conversion and reaches values of up to 10 branches per 10^4 C atoms.
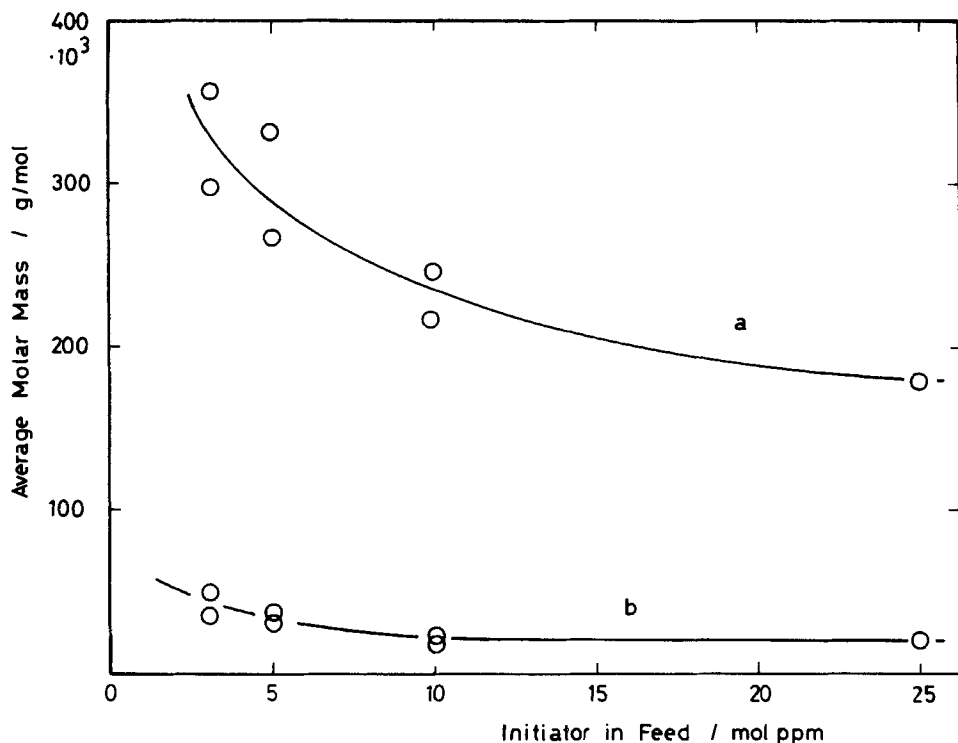
FIG. 5. Average molecular weight. Curve a: Weight-average. Curve b: Number-average. Pressure, 1700 bar; temperature, 260°C; residence time, 60 s.

CONCLUSIONS

The initiator consumption of the asymmetrically substituted bifunctional peroxide compared in Fig. 8 with that of the symmetrical bifunctional per-oxides investigated previously. For this purpose, the initiator consumption of Peroxide I was interpolated for a 20 mol ppm initiator concentration in the feed from the values for 25 and 10 mol ppm (Fig. 8, Curve d). The initi-ator consumption/temperature characteristics of the asymmetrical bifunc-tional Peroxide I are very similar to those of the symmetrical bifunctional Peroxides III and IV. This is clearly shown by the data in Table 1. The se-quence remains unaffected even if the initiator consumption is expressed in
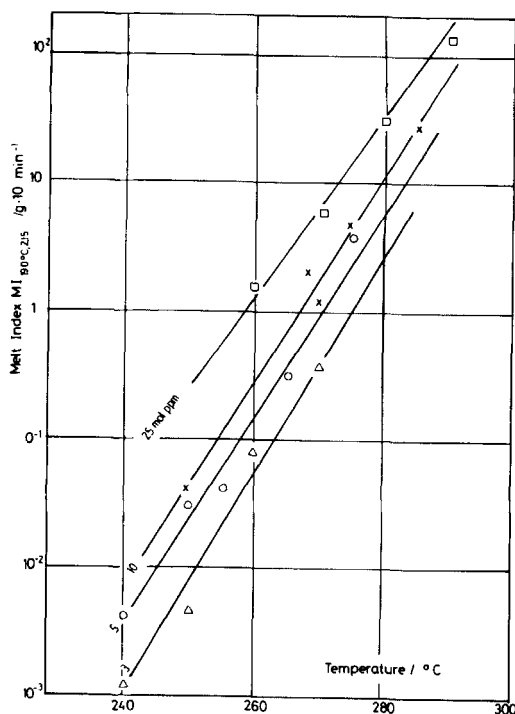
FIG. 6. Melt index as a function of polymerization temperature. Pressure, 1700 bar; residence time, 60 s.

moles instead of units of weight, which is more meaningful to the user. Replacing an ester group in the bis perpivalate (II) by a t-butyl group leads to greater thermal stability of the bifunctional Peroxide I. Its optimal temperature is only 10°C below that of Peroxide IV with one t-butyl radical each on the O—O groups.

It has again been confirmed that the peroxide consumption per kg polyethylene produced does not necessarily correlate with the content of active oxygen. At the same level of consumption, the bifunctional Peroxide III has a much higher active oxygen content (13.7% based on pure peroxide) than Peroxide I (10%) or Peroxide IV (11.0%). With an active oxygen content of 11.0%, the monofunctional di-t-butyl peroxide has an even lower minimum consumption (0.6 g initiator/kg PE) under the same polymeriza-
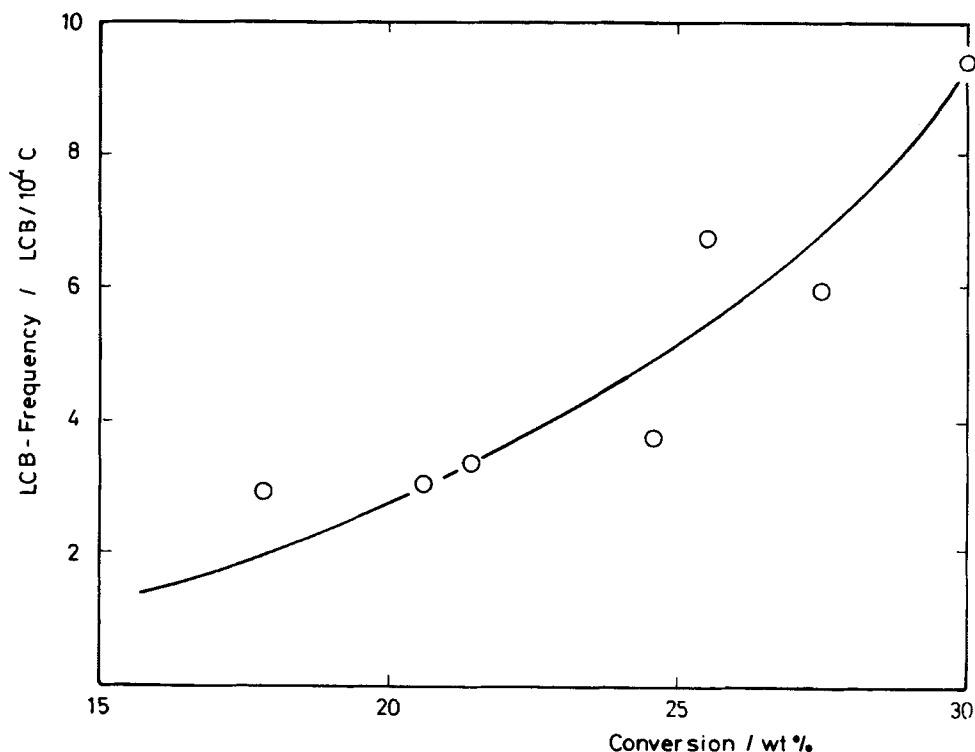
FIG. 7. Long-chain branching frequency. Pressure, 1700 bar; temperature, 260°C; residence time, 60 s.

tion conditions. Consequently, neither symmetrically nor asymmetrically substituted bifunctional peroxides have the expected [3] consumption advantage compared to monofunctional compounds.

The flat consumption minimum of the asymmetrically substituted bifunctional Peroxide I is an indication of the different levels of thermal stability of the two O—O bonds in the peroxide molecule. In the case of Peroxide I, this difference is not sufficiently large to be able, as suggested [4], to cover the entire temperature range in an industrial tubular or autoclave reactor with a single initiator.

An aspect of great interest from the practical point of view is the slightly higher polymer polydispersity of 7 to 10 which was achieved with asymmetrically substituted bifunctional peroxide. The higher polydispersity results
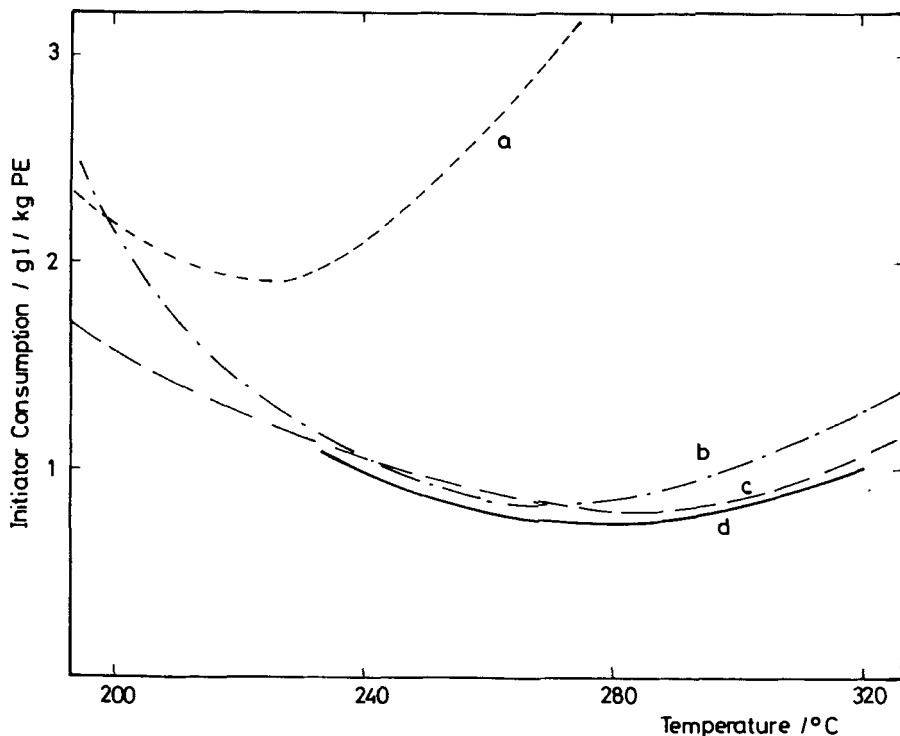
FIG. 8. Comparison of the consumption of different difunctional peroxides. Pressure, 1700 bar; residence time, 60 or 40 s; initiator concentration, 20 mol ppm. Curve a, Peroxide II. Curve b, Peroxide III. Curve c, Peroxide IV. Curve d, Peroxide I.

from the bimodal molecular weight distribution, which was also observed with symmetrically substituted bifunctional peroxides. The polydispersity of a polyethylene prepared under the same conditions with a monofunctional peroxide initiator is less than 7 [5]. In order to achieve the same polydispersity with a *t*-butyl perpivalate as that obtained with Peroxide I, the reactor temperature would have to be reduced to around 200°C with a consequent loss of yield.

TABLE 1. Minimum Initiator Consumption and Optimal Temperature for Application[a]

Peroxide	Minimum initiator consumption		Optimum temperature, °C
	g/kg PE	mmol/kg PE	
I 2,5-Dimethylhexane-2-*t*-butylperoxy-5-perpivalate	0.74	2.33	273
II 2,5-Dimethylhexane-2,5-bis perpivalate	1.9	5.49	235
III 2,2-Bis(*t*-butylperoxy)-butane	0.82	3.50	268
IV 2,5-Dimethylhexane-2,5-di-*t*-butyl peroxide	0.80	2.76	287

[a]Pressure, 1700 bar; residence time, 40 and 60 s; initiator concentration in the feed, 20 mol ppm.

REFERENCES

[1] G. Luft and H. Seidl, *Angew. Makromol. Chem., 129,* 61 (1985).
[2] G. Luft, P.-Ch. Lim, S. Pavlakis, and H. Seidl, *J. Macromol. Sci.–Chem., A22*(9), 1183 (1985).
[3] J. E. Guillet and E. B. Towne, German DOS 1,213,998 (1966), to Eastman Kodak, USA.
[4] M. Rätzsch, F. Gärtner, and R. Kilian, German DOS 1,645,618 (1970), to VEB Leuna-Werke, Walter Ulbricht.
[5] G. Luft and N. Fischer, *Macromol. Chem.,* In Press.