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Properties of Low-Density Polyethylene Produced with Organic Peroxides Together with Oxygen

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ABSTRACT

Both organic peroxides and molecular oxygen can be used for the high-pressure polymerization of ethylene. In order to answer the question if the product quality is influenced by the choice of the initiator, polyethylenes were produced in a stirred autoclave under 1700 bar at temperatures of 200-320°C with DTBP, oxygen, and with mixtures of both initiators. The products were compared for density, short- and long-chain branching, the average molar mass, and the molar mass distribution. Except for a slight increase in the number of long-chain branches, and as a consequence of this a slightly broader molar mass distribution, no significant changes of product properties could be noted. There are no objections against the combined use of peroxide and oxygen; for example, when the conversion from oxygen to peroxide takes place.

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INTRODUCTION

In the modern processes of high-pressure polymerization of ethylene, several initiators are fed into the reactor which are active in different temperature ranges. Some patent specifications claim the application of organic peroxides in combination with molecular oxygen. Representative of the aforesaid are the patent specifications [1-3] in which other references are cited.

In tubular reactors peroxide and oxygen, mostly in the form of air oxygen, can be introduced at the injection point, e.g., at the beginning of the reaction zone. Preferably the initiators are introduced separately into different zones of the reactor, e.g., a peroxide with a short half-life time can be injected in the first reactor zone and oxygen into a second zone. Another more stable peroxide which has a longer half-life time can be introduced into a further zone.

In some of our earlier examinations [4] the interaction with peroxide and oxygen initiation in the high-pressure polymerization and their effect on the conversion in the reactor were elucidated. In this work we wanted to examine if the properties of the polyethylene produced with peroxide/oxygen differed from those products manufactured with peroxide or oxygen only.

EXPERIMENTAL

The polyethylenes were produced in a continuously operating stirred autoclave under a pressure of 1700 bar and temperatures between 200 and 320°C. The residence time was 40 s. The same equipment and technique were used as for previous investigations [5]. Di-tert-butyl peroxide (DTBP) was used as initiator. The temperature giving a half-life of 1 min is 190°C for this peroxide. The DTBP was dissolved in isododecane and was mixed with the ethylene passing into the reactor of a concentration of 10 mole ppm. At the same time 18 to 80 mole ppm oxygen was also metered into the reactor.

The density, the short- and long-chain branching, the average molar mass, and the molar mass distribution were determined on the polyethylene produced under steady-state conditions.

The density was measured on pressed films using the suspension method at 25°C in an isopropanol-water mixture. The films, 0.02 mm thick, were heat-treated beforehand at 120°C and chilled with ice-cold water.

The short-chain branching was determined on films 0.01 to 0.1 mm thick using IR and NMR spectroscopy. The CH_3 deformation vibration at 7.25 μm was used to evaluate the infrared spectroscopic measurements, and the overlapping of amorphous regions at 7.3 and 7.4 μm caused by the CH_2 vibration was compensated for by means of a wedge-shaped film of polyethylene in the reference beam.

For the unfractionated samples, the weight-average number n_w of the branching points per molecule was determined from the relation which applies to polydisperse systems [6, 7]:

$$g(P) = \frac{6}{n_w}\left(1/2\left(\frac{2 + n_w}{n_w}\right)^{0.5} \ln \frac{(2 + n_w)^{0.5} + n_w^{\ 0.5}}{(2 + n_w)^{0.5} - n_w^{\ 0.5}} - 1\right)$$

The ratio of the intrinsic viscosity η_{br} of the branched eluate fractions to the intrinsic viscosity η_{lin} of a linear, i.e., unbranched, polyethylene with the same average molar mass was used to obtain

$$\eta_{br}/\eta_{lin} = g^b$$

Applying Kuhn's theory [8, 9], a value of b = 1.2 was used for exponent b for the polymers obtained from the agitated vessel reactors which were branched in a bushlike fashion.

The intrinsic viscosities from which the average molar mass can be determined by means of the Mark-Houwink relation $[\eta] = KM^a$ were measured both in tetralin and in 1,2,4-trichlorobenzene. Different values for the parameters K and "a" have to be used depending on the solvent and measuring temperature. An Ubbelohde viscometer was used. Three solutions with concentrations of 0.07, 0.15, and 0.22 g/dL were prepared from one sample and the intrinsic viscosity was calculated at 135°C from the average of 4 flow measurements by extrapolation to infinite dilution. A Hagenbach-Couette correction was unnecessary because the flow times were always more than 100 s. The intrinsic viscosities were required mainly for determining long-chain branching.

The number-average molar mass of the samples was determined by means of a commercially available membrane osmometer (Knauer, Berlin). With a measuring cell temperature of 125°C, the polymer solutions with a concentration between 0.1 and 0.4 mg/mL were analyzed and the osmotic limiting pressure determined by extrapolation to zero concentration. Vacuum-distilled tetralin and tetralin purified by column chromatography were used as the solvents. The membrane was made of regenerated cellulose.

Gel permeation chromatography was used to measure the molar mass distribution. It contained 5 semipreparative columns which had been filled with inorganic material of the Lichrospher 60, 100, 500, 1,000, and 4,000 Å type. This made it possible to reach operating temperatures of up to 150°C and pressures of 100-150 bar. Tetrahydronaphthalene was used as the eluant. Due to the high elution rates of 0.7 to 1.5 mL/min, the analysis time was 20-30 min.

RESULTS

The densities of the polyethylenes produced with both organic peroxide and oxygen are plotted against the polymerization temperature in Fig. 1. The samples produced with a combination of DTBP and oxygen are marked with the filled-in symbols, while those produced with only oxygen initiation are the open symbols. The total initiator concentration, with both the mixed initiator system and with pure oxygen, were specifically kept the same in these trials. For comparison, the densities of samples produced with organic peroxides, including DTBP, at a concentration of 40 mole ppm are also plotted (dashed line). The figures are taken from other investigations [10] concerning the influence of synthesis conditions on the structure of low-density polyethylene.

The density significantly decreases with increasing polymerization temperature. Higher initiator concentrations result in lower densities. The density is therefore independent of whether the initiation is by pure organic peroxide, pure oxygen, or a mixture of both.

This also applies to the amount of short-chain branching. This is plotted against the polymerization temperature in Fig. 2. The number of short-chain branches increases independently of the nature of the initiation system, this increasing with polymerization temperature.

Certain trends are indicated when the number of long-chain branches is plotted. In Fig. 3 the values of samples produced with the mixed initiators (symbols ▲ ● ■) and pure oxygen (symbols △ ○ □) are plotted together with the range of long-chain branching, resulting from initiation with pure peroxide initiation (dashed-line curve).

Apparently the number of long-chain branches in samples produced with the mixed peroxide/oxygen initiator is near the upper limit, whereas the pure oxygen-produced samples are near the lower limit.

For the number-average molar mass, again only the total initiator concentration is important. Apart from that, the known dependencies are unchanged. The average molar mass decreases at the same synthesis pressure with increasing polymerization temperature and initiator concentration (Fig. 4).

In Fig. 5 the integral molar mass distributions for the products are given; these were obtained in three series of trials at different temperatures. The data in the upper diagram (a) were measured on the products obtained from the polymerization trials with 40 mole ppm DTBP. The distribution curves (c) were determined from the products polymerized with 50 mole ppm of oxygen, and the middle diagram (b) for the products polymerized with 10 mole ppm DTBP and 37 mol ppm oxygen. The distribution curves of the polyethylenes produced at higher temperatures extend over a smaller molar mass region, i.e., the distribution narrowed with higher polymerization temperatures. These dependencies, especially significant in the lower diagram (c), were clearly known. At nearly the same initiator concentration (10 mole ppm DTBP, 37 mole ppm oxygen), the curves of the middle diagrams are somewhat broader than the curves in (c).

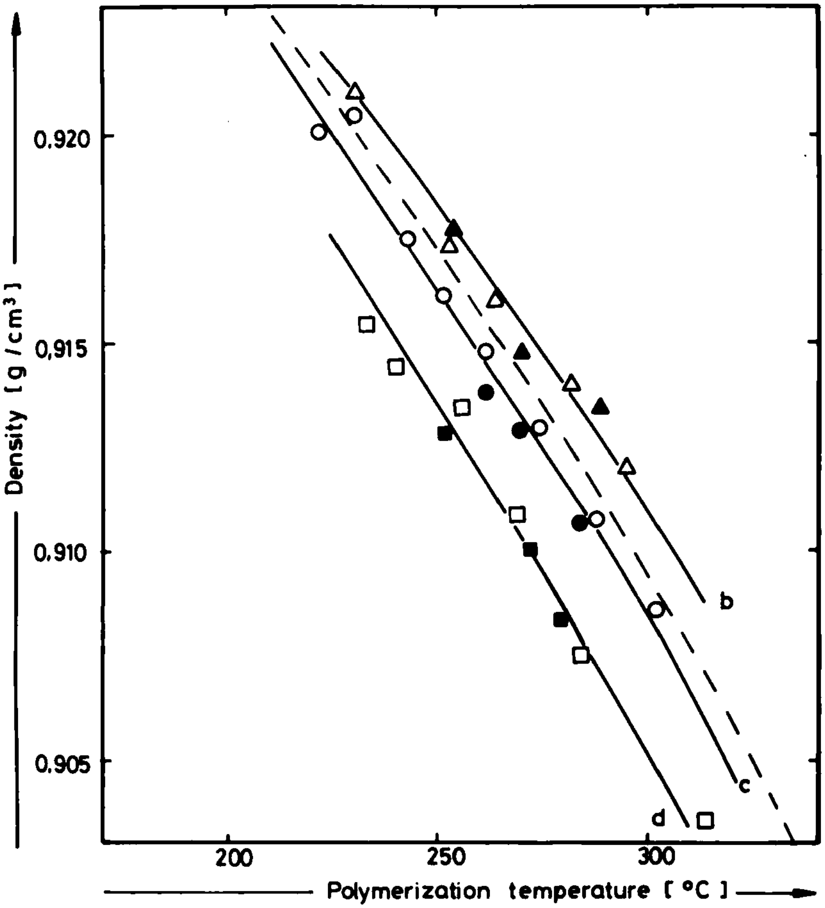

FIG. 1. Density. Pressure, 1700 bar; residence time 40 s; (- -) 40 mole ppm peroxides.

Curve	Symbol	DTBP [mole ppm]	Oxygen [mole ppm]
b	▲	10	18
b	△	-	30
c	●	10	37
c	○	-	50
d	■	10	60
d	□	-	80

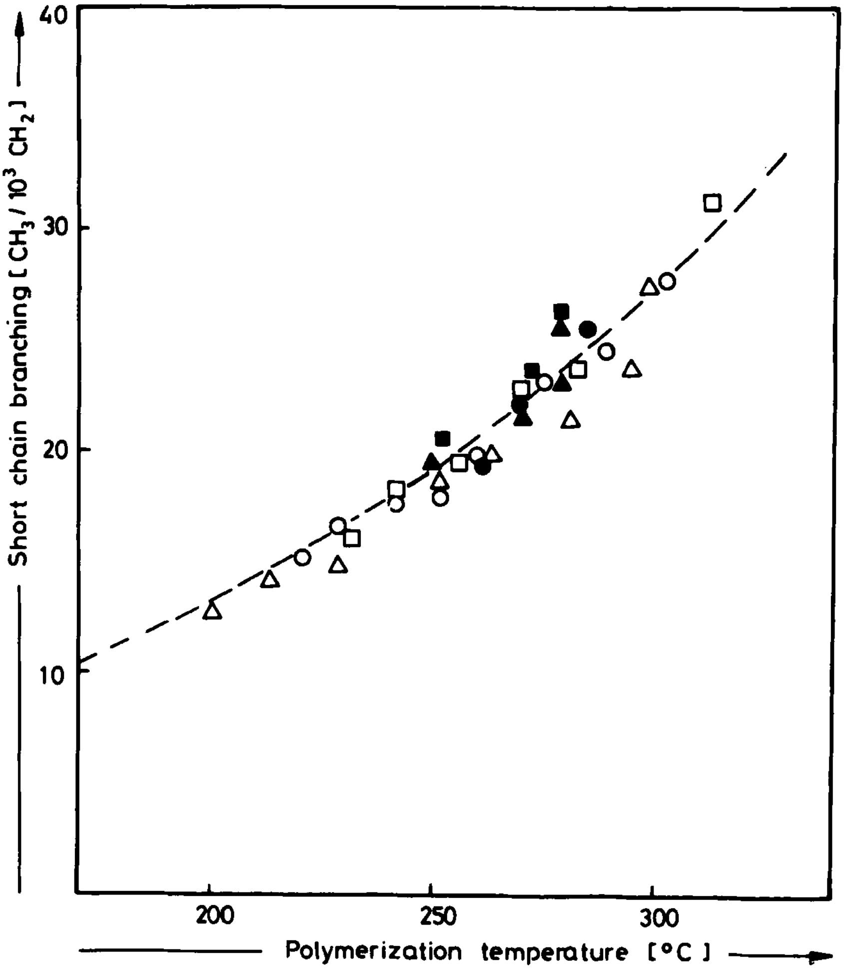

FIG. 2. Short chain branching. Pressure, 1700 bar; residence time, 40 s; (- -) 40 mole ppm peroxides.

Symbol	DTBP [mole ppm]	Oxygen [mole ppm]
▲	10	18
△	-	30
●	10	37
○	-	50
■	10	60
□	-	80

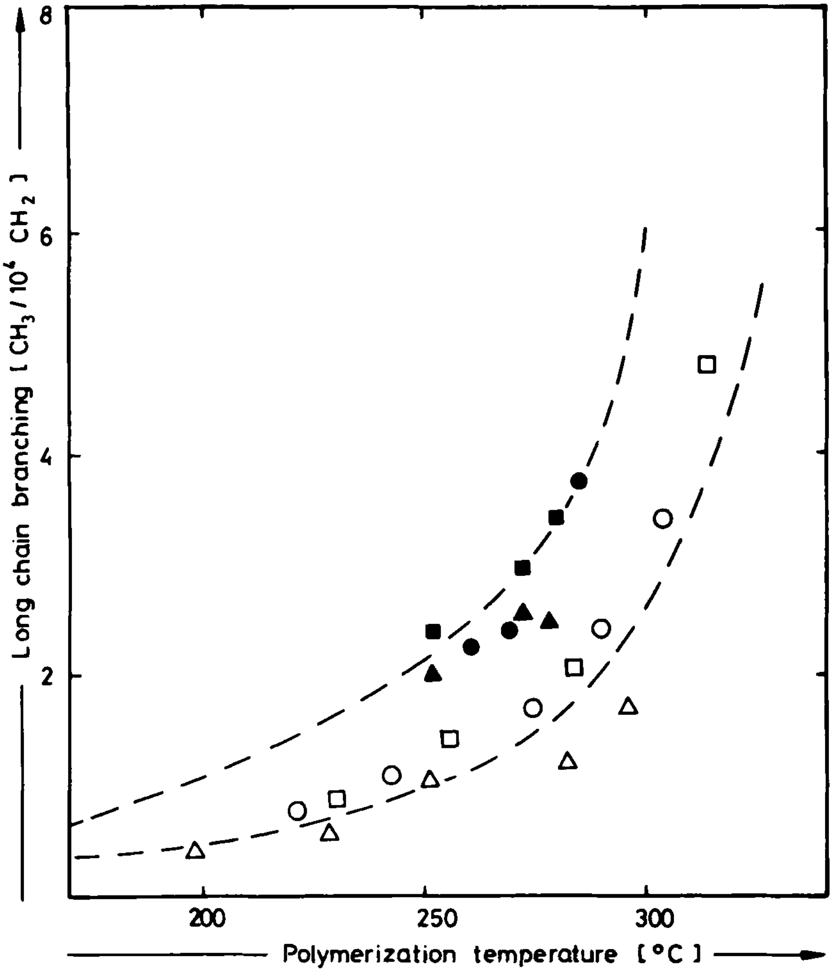

FIG. 3. Long-chain branching. Pressure, 1700 bar; residence time, 40 s; (- -) 40 mole ppm peroxides.

Symbol	DTBP [mole ppm]	Oxygen [mole ppm]
▲	10	18
△	-	30
●	10	37
○	-	50
■	10	60
□	-	80

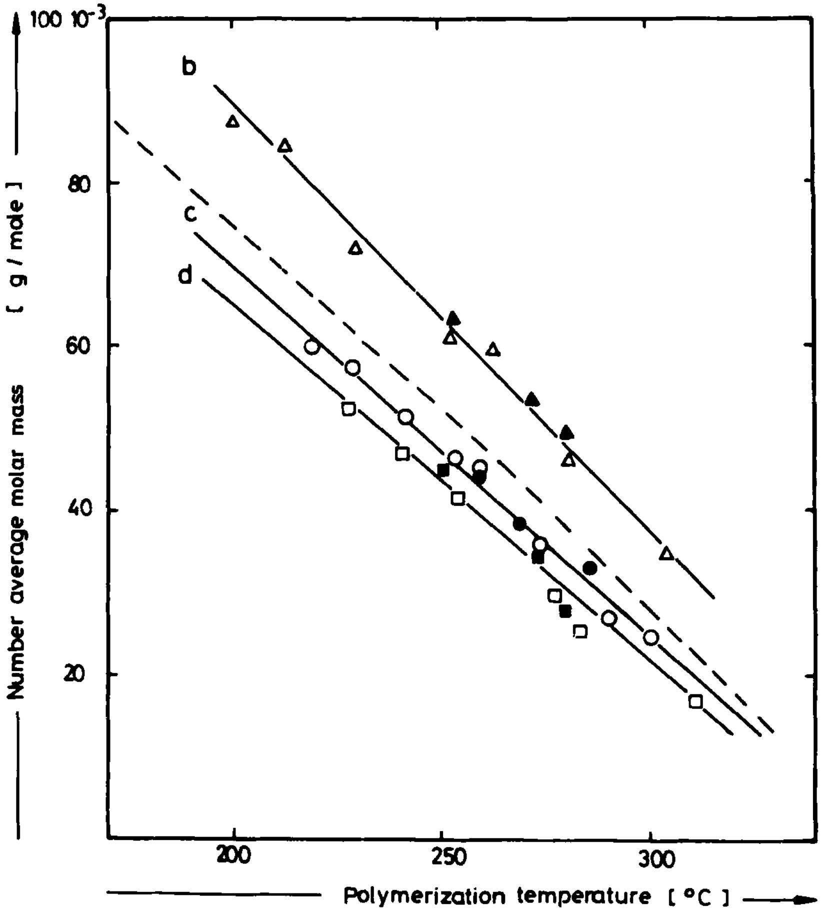

FIG. 4. Number-average molar mass. Pressure 1700 bar; residence time, 40 s; (- -) 40 mole ppm peroxides.

Curve	Symbol	DTBP [mole ppm]	Oxygen [mole ppm]
b	▲	10	18
b	△	-	30
c	●	10	37
c	○	-	50
d	■	10	60
d	□	-	80

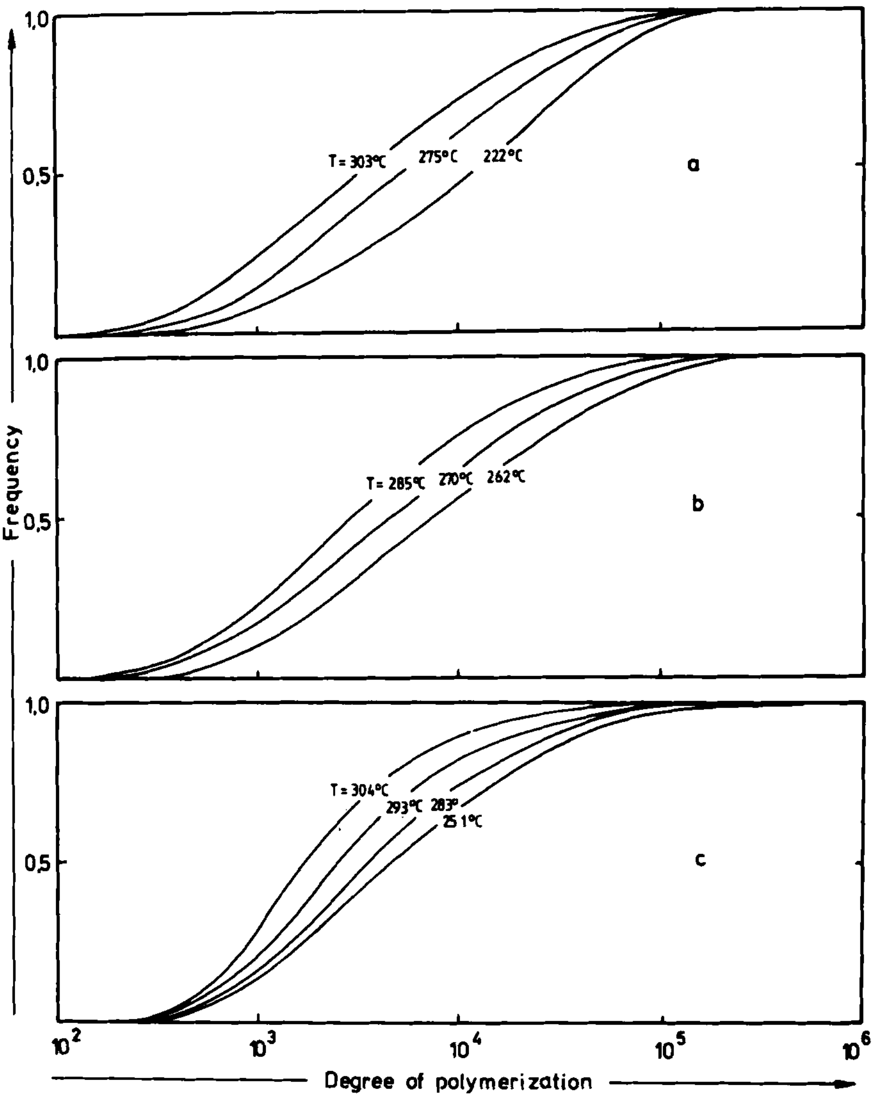

FIG. 5. Molar mass distribution. Pressure, 1700 bar; residence time, 40 s.

Curve	DTBP [mole ppm]	Oxygen [mole ppm]
a	40	
b	10	37
c		50

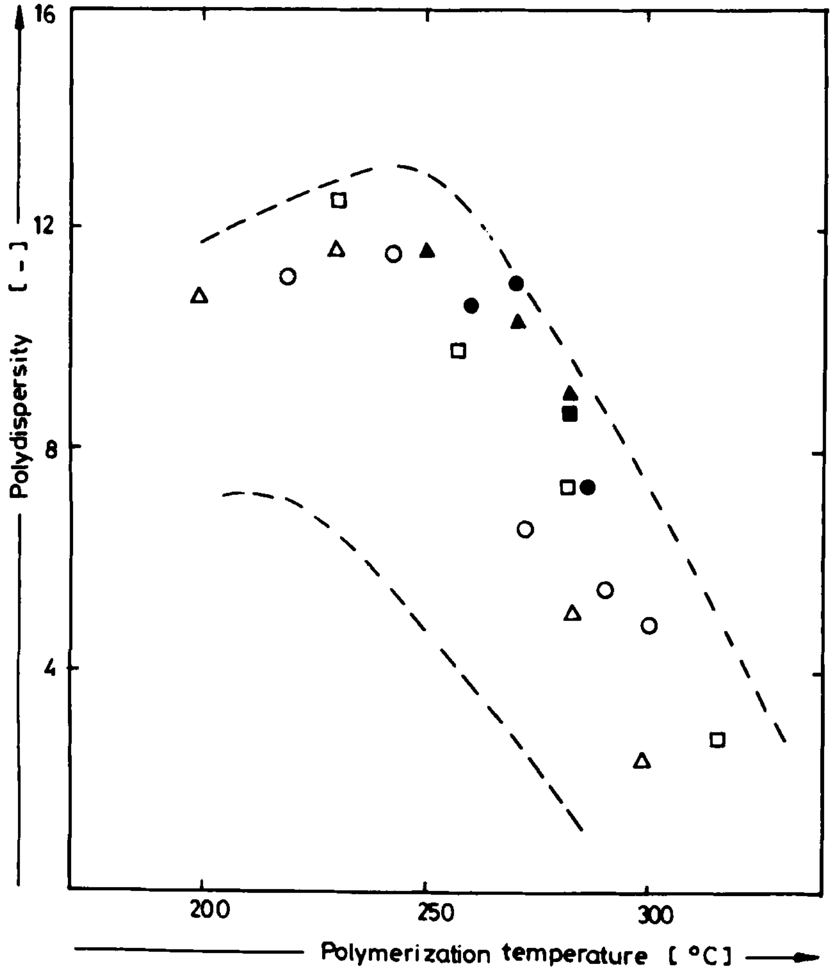

FIG. 6. Polydispersity. Pressure, 1700 bar; residence time, 40 s.

Symbol	DTBP [mole ppm]	Oxygen [mole ppm]
▲	10	18
△	-	30
●	10	37
○	-	50
■	10	60
□	-	80

The dependencies observed for the molar mass distribution are reflected in the polydispersity, which is calculated as a quotient of mass average molar mass to the number-average molar mass. The polydispersity decreases in the region of 200-320°C (Fig. 6) with increasing polymerization temperature.

The products made with simultaneous injection of oxygen and peroxide have polydispersities in the upper region of the measured band.

CONCLUSIONS

A comparison of the polyethylenes produced with the different initiators proves that simultaneous injection of both peroxide and oxygen does not show any significant difference in the product quality. This is essentially determined from the polymerization temperature (and the pressure). In technical tubular reactors, however, the joint application of peroxide and oxygen can, according to the point of injection, change the temperature profile and lead to variations in the product quality.

The slight increase in the number of long-chain branches, which could be observed with the peroxide-oxygen initiation at constant temperature, should not be overestimated. This increase might be responsible—with the number-average molar mass being unchanged—for the increase of the average molar mass, and consequently for the slight increase of the polydispersity.

There are no objections against the simultaneous introduction of peroxide and oxygen; for example, during converting some processes from oxygen to peroxide initiation. On the other hand, this is not absolutely necessary.

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