PROCESS FOR MANUFACTURING POLYETHYLENE

Abstract: Process for manufacturing a polyethylene homo- or copolymer by conducting high-pressure polymerization of ethylene, optionally in combination with one or more co-monomers, in a tubular reactor, wherein tert-amyl peroxidebutyrate is used as polymerization initiator.
PROCESS FOR MANUFACTURING POLYETHYLENE

The present invention relates to a process for manufacturing polyethylene by high-pressure polymerization in a tubular reactor.

Low density polyethylene (LDPE) is generally made by high pressure polymerization in either an autoclave reactor (a high pressure continuously stirred tank reactor) or a tubular reactor. The choice of reactor affects the properties of the LDPE. The extent of branching of "autoclave LDPE" is higher than of "tubular LDPE". This is due to the residence time in the reactors. A tubular reactor operates under plug flow conditions, meaning that the entire reaction mixture has the same residence time. In autoclave reactors, back mixing results in a spread of residence times. The result is a higher degree of branching of autoclave LDPE compared to tubular LDPE.

In order to obtain clear LDPE sheets, the extent of branching of the LDPE - expressed as the branching number Bn (number of branches per molecule) - should be relatively low, preferably below 15, more preferably below 10. The branching number of autoclave LDPE is generally above 15, whereas the branching number of tubular LDPE is generally below 10. Tubular LDPE is therefore preferred for preparing clear LDPE sheets.

Apart from the type of reactor, also the type of polymerization initiator affects the extent of branching. Initiators that result in mainly H-abstraction instead of addition to monomer will induce more branching.

Organic peroxides having an alkyl group on one side of the peroxy function (most commonly either a tert-butyl or tert-amyl group) form alkoxy radicals upon dissociation. This alkoxy radical can either abstract a hydrogen atom to form an alcohol:
or undergo β-scission to yield a ketone and an alkyl radical:

$$\text{O}$$

$$\text{OH}$$

Organic peroxides that decompose into aggressive radicals like O-radicals and methyl radicals, mainly abstract hydrogen atoms, thereby forming alcohols and methane, respectively.

For the production of clear LDPE sheets, the amount of hydrogen abstraction should be relatively low.

Organic peroxides that are frequently used for the polymerization of ethylene are peroxyesters like tert-butyl peroxy-2-ethylhexanoate and tert-amyl peroxy-2-ethylhexanoate:
Of these peroxides, tert-butyl peroxy-2-ethylhexanoate forms an aggressive methyl radical upon β-scission, whereas tert-amyl peroxy-2-ethylhexanoate gives the more selective ethyl radical. Hence, tert-amyl peroxy-2-ethylhexanoate gives less hydrogen abstraction than tert-butyl peroxy-2-ethylhexanoate.

It has now surprisingly been found that hydrogen abstraction can be further reduced by using tert-amyl peroxyisobutyrate as initiator:

![Chemical Structure](image)

This is surprising because this peroxide forms the same tert-amyloxy radical as tert-amyl peroxy-2-ethylhexanoate.

In addition, it has been found that tert-amyl peroxyisobutyrate has a higher efficiency than tert-butyl peroxy-2-ethylhexanoate and tert-amyl peroxy-2-ethylhexanoate in terms of reduced termination reactions of primary radicals inside the solvent cage.

Hence, this peroxide is able to produce polyethylene with a low degree of branching which is very suitable for preparing clear polyethylene films.

The present invention therefore relates to a process for manufacturing a polyethylene homo- or copolymer by conducting high-pressure polymerization of ethylene, optionally in combination with one or more co-monomers, in a tubular reactor, wherein tert-amyl peroxyisobutyrate is used as polymerization initiator.
The polymerization is carried out at pressures that are preferably in the range 500-5000 bar, more preferably 1500-3500 bar, and most preferably 2000-3300 bar.

The reaction temperature is preferably in the range 100-350 °C, more preferably 130-330 °C, and most preferably 160-320 °C.

Tert-amyl peroxyisobutyrate can be dosed to the reactor 100% pure or, more preferably, as a solution in hydrocarbons, such as odorless mineral spirit, isododecane, or one or more reactive diluents. A reactive diluent is a liquid unsaturated hydrocarbon that can copolymerize with ethylene. Examples of reactive diluents are olefins, more preferably C₅₋₁₂ alpha-olefins. The tert-amyl peroxyisobutyrate concentration in such solution is preferably in the range 5-50 wt%, more preferably 10-30 wt%.

According to the present invention, tert-amyl peroxyisobutyrate is preferably added to the reactor in amounts of 100 to 1000 ppm (weight parts per million), more preferably 100-500 ppm, calculated as pure peroxide and based on the weight of polyethylene.

The process of the present invention can be used both for the homopolymerization of ethylene and for the co-polymerization of ethylene with other monomers, provided that these monomers undergo free-radical polymerization with ethylene under high pressure. Examples of suitable co-polymerizable monomers are α,β-ethylenically unsaturated Cs-Ce-carboxylic acids (e.g. maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid, or crotonic acid), α,β-ethylenically unsaturated C₃₋₁₅-carboxylic esters or anhydrides (e.g. methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, or tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methacrylic anhydride, maleic anhydride or itaconic anhydride), α-olefins (e.g. propene, 1-butene, 1-pentene, 1-hexene, 1-octene, or 1-decene). In addition, it is possible to use vinyl carboxylates, particularly preferably vinyl acetate, as co-monomers.
The proportion of co-monomers in the reaction mixture is preferably in the range 0-45 wt%, more preferably 3-35 wt%, based on the weight of ethylene monomer. Most preferably, the process is used for the manufacture of ethylene homopolymer, more in particular low density polyethylene homopolymer.

The polymer resulting from the process of the present invention preferably has a density in the range 910-940 kg/m$^3$, more preferably 918-926 kg/m$^3$ and most preferably 920-925 kg/m$^3$. The density is mostly controlled by the reactor pressure and temperature profile and can also be influenced by means of the chain regulators and/or co-monomers.

Low density polyethylene (LDPE) is defined as having a density in the range 0.910-0.940 g/cm$^3$.

The melt flow index of the resulting polymer in accordance with DIN 53 735 (190°C/2.16 kg) is preferably less than 50 g/10 min, more preferably less than 10 g/10 min, and most preferably less than 5 g/10 min.

In a preferred embodiment, polymerization initiator(s) is/are introduced into the tubular reactor along the length of the tube at from 1 to 6 inlet points, so that from 1 to 6 reaction zones are obtained in which polymerization is initiated. More preferably 2-6, and most preferably 3-5 initiator inlet points are used and preferably 2-6, and most preferably 3-5 reaction zones are created. Tert-amyl peroxyisobutyrate is introduced in at least one of the reaction zones. It preferably is introduced in a plurality of reaction zones. Most preferably, it is introduced in every reaction zone.

In addition to tert-amyl peroxyisobutyrate, one or more co-initiators can be used in the process of the present invention. In a preferred embodiment, one such co-initiator has a higher reactivity (i.e. shorter half-life) and one or more, preferably one or two, of such co-initiators has/have a lower reactivity (i.e. longer half-life) than tert-amyl peroxyisobutyrate at a specific temperature.
Examples of co-initiators with a higher reactivity than tert-amyl peroxylsobutyrate are di(2-ethylhexyl)peroxydicarbonate, tert-butyl peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-amyl peroxyisobutyrate, and tert-butyl peroxyisobutyrate. Tert-butyl peroxyisobutyrate is a highly preferred co-initiator with higher reactivity, especially for the production of ethylene homopolymers. For the production of ethylene co-polymers, di(2-ethylhexyl)peroxydicarbonate and tert-butyl peroxyneodecanoate are highly preferred co-initiators with higher reactivity.

Examples of co-initiators with a lower reactivity than tert-amyl peroxylsobutyrate are tert-butyl peroxy-3,3,5-trimethylhexanoate, tert-butyl peroxybenzoate, 2,2-di(tert-butylperoxy)butane, tert-butyl peroxycetate, tert-butyl peroxy isopropyl carbonate, di-tert-butyl peroxide, and 3,3,5,7,7-pentamethyl-1,2,4-trioxepane. Di-tert-butyl peroxide and tert-butyl peroxy-3,3,5-trimethylhexanoate are a highly preferred co-initiators with lower reactivity, with di-tert-butyl peroxide being the most preferred.

Specifically preferred combinations of initiators for use in the process of the present invention are:

- the combination of tert-butyl peroxyisobutyrate, tert-amyl peroxyisobutyrate, tert-butyl peroxy-3,3,5-trimethylhexanoate, and di-tert-butyl peroxide,
- the combination of tert-butyl peroxyisobutyrate, tert-amyl peroxyisobutyrate, tert-butyl peroxybenzoate, and di-tert-butyl peroxide,
- the combination of tert-butyl peroxyisobutyrate, tert-amyl peroxyisobutyrate, 2,2-di(tert-butylperoxy)butane, and di-tert-butyl peroxide,
- the combination of tert-butyl peroxyisobutyrate, tert-amyl peroxyisobutyrate, tert-butyl peroxycetate, and di-tert-butyl peroxide,
- the combination of tert-butyl peroxyisobutyrate, tert-amyl peroxyisobutyrate, tert-butyl peroxybenzoate, and tert-butyl peroxy-3,3,5-trimethylhexanoate,
- the combination of tert-butyi peroxypivaiate, tert-amyi peroxyisobutyrate, tert-butyi peroxyacetate, and tert-butyi peroxy-3,3,5-trimethyihexanoate,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, tert-butyi peroxy-3,3,5-trimethyihexanoate, and di-tert-butyi peroxide,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, tert-butyi peroxybenzoate, and di-tert-butyi peroxide,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, 2,2-di(tert-butyi peroxy)butane, and di-tert-butyi peroxide,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, tert-butyi peroxyacetate, and di-tert-butyi peroxide,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, tert-butyi peroxybenzoate, and tert-butyi peroxy-3,3,5-trimethyihexanoate,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, 2,2-di(tert-butyi peroxy)butane, and tert-butyi peroxy-3,3,5-trimethyihexanoate,
- the combination of di(2-ethyihexyl)peroxydicarbonate, tert-amyi peroxyisobutyrate, tert-butyi peroxybenzoate, and tert-butyi peroxy-3,3,5-trimethyihexanoate,
- the combination of tert-butylperoxyneodecanoate, tert-amyl peroxyisobutyrate, 2,2-di(tert-butylperoxy)butane, and tert-butyl peroxy-3,3,5-trimethylhexanoate,
- the combination of tert-butylperoxyneodecanoate, tert-amyl peroxyisobutyrate, tert-butyl peroxyacetate, and tert-butyl peroxy-3,3,5-trimethylhexanoate.

In one embodiment, the total amount of monomer - and, if desired, co-monomer - is introduced at the reactor inlet. In another embodiment, the tubular reactor has at least two reaction zones into each of which additional cold or pre-heated monomer and/or cold or pre-heated co-monomer is/are introduced as a fresh gas stream before the beginning of each reaction zone. Preference is given to at least three successive reaction zones.

Examples of suitable tubular reactors are disclosed in US 4,135,044 and 4,175,169. These reactors have a comparatively small tube diameter in each reaction zone from the introduction point for initiator to the temperature maximum, compared to the enlarged tube diameter in the subsequent cooling zone (from the temperature maximum to the next introduction point for initiator).

This enables a high conversion to be achieved at a relatively low pressure drop over the length of the reactor.

The tubular reactor is usually provided with a cooling jacket to remove the reaction heat.

The ratio of length-to-diameter of the tubular reactor is preferably in the range 10000-50000, more preferably 15000-35000.

The mean residence time of the reaction mixture in the tubular reactor is generally in the range 30-300 seconds, more in particular 30-120 seconds.

In the process of the present invention, the molar mass of the polyethylene to be prepared can be regulated in conventional ways by the addition of molecular weight regulators. Examples of such regulators are aliphatic and olefinic
hydrocarbons (e.g. pentane, hexane, cyclohexane, propene, pentene, or hexene), ketones (e.g. acetone, diethyl ketone, or diamyl ketone), aldehydes (e.g. formaldehyde or acetaldehyde), and saturated aliphatic alcohols (e.g. methanol, ethanol, propanol, or butanol). Particular preference is given to using saturated aliphatic aldehydes, in particular propionaldehydes, or olefins such as propene or hexene. The molecular weight regulator is preferably added to the reaction mixture upstream of the tubular reactor or together with the polymerization initiator at the various inlet points along the reactor.

After the last introduction of polymerization initiator, the reaction mixture is cooled in order to allow discharge of the product from the reactor. The reaction mixture is ejected at the outlet end of the tubular reactor by means of an appropriate high-pressure let-down valve system. After discharge of the reaction mixture, the polymer is separated from any unreacted monomers by depressurization, after which the monomers can be re-circulated to the reactor.

The resulting polyethylene is highly suitable to make polyethylene films and film products.

EXAMPLE

In this example, the decomposition of tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, and tert-amyl peroxyisobutyrate under conditions comparable to those in an ethylene polymerization process was studied.

Solutions of the peroxides in n-nonane (0.1 M) were prepared and the peroxides were completely decomposed in a continuous flow reactor at a temperature of 175°C and a pressure of 2000 bar.

To compare the selected peroxides, the amount of acetone formed during total decomposition was taken as a measure for the amount of β-scission. The results are displayed in Table 1, which shows that tert-amyl peroxyisobutyrate undergoes significantly more β-scission than the other two peroxides. Tert-amyl
peroxyisobutyrate thus forms a higher number of selective alkyl-radicals and gives reduced hydrogen abstraction. This will result in less branching.

Table 1

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<th>Acetone (mol/mol peroxide)</th>
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<tr>
<td>tert-amylperoxy isobutyrate</td>
<td>0.515</td>
</tr>
<tr>
<td>tert-butylperoxy 2-ethylhexanoate</td>
<td>0.094</td>
</tr>
<tr>
<td>tert-amylperoxy 2-ethylhexanoate</td>
<td>0.301</td>
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The in-cage termination reactions affect the efficiency of peroxides. If the radicals that are formed upon peroxide dissociation are directly consumed inside the solvent cage to form ethers (through in-cage decarboxylation) and alkenes (through in-cage disproportionation), the efficiency drops, simply because these radicals are not available for polymerization initiation. Hence, the formation of alkenes and ethers is an indicator for the efficiency.

Table 2

<table>
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<th>Ether (mol/mol peroxide)</th>
<th>Alkene (mol/mol peroxide)</th>
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<tr>
<td>tert-amylperoxy isobutyrate</td>
<td>0.13</td>
<td>0.03</td>
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<tr>
<td>tert-butylperoxy 2-ethylhexanoate</td>
<td>0.14</td>
<td>0.42</td>
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<tr>
<td>tert-amylperoxy 2-ethylhexanoate</td>
<td>0.21</td>
<td>0.37</td>
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</table>

Table 2 shows that tert-amyl peroxyisobutyrate gives less in-cage reactions than the other two peroxides, indicating a higher efficiency.
CLAIMS

1. Process for manufacturing a polyethylene homo- or copolymer by conducting high-pressure polymerization of ethylene, optionally in combination with one or more co-monomers, in a tubular reactor, wherein tert-amyl peroxyisobutyrate is used as polymerization initiator.

2. Process according to claim 1 wherein the polymerization is conducted at a temperature in the range 160-350°C.

3. Process according to claim 1 or 2 wherein the polymerization is conducted at a pressure in the range 500-5000 bar.

4. Process according to any one of the preceding claims wherein the polyethylene is low density polyethylene (LDPE).

5. Process according to any one of the preceding claims, wherein one or more co-initiators are used.

6. Process according to claim 5, using, as co-initiator, a peroxide selected from the group consisting of di(2-ethylhexyl)peroxydicarbonate, tert-butyi peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-amyl peroxypivalate, and tert-butyl peroxypivalate.

7. Process according to claim 6 wherein the co-initiator is tert-butyi peroxypivalate.

8. Process according to claim 6 wherein the co-initiator is di(2-ethylhexyl)peroxydicarbonate or tert-butyl peroxyneodecanoate.

9. Process according to any one of claims 5-8, using, as co-initiator, a peroxide selected from the group of tert-butyl peroxy-3,3,5-
trimethyhexanoate, tert-butyl peroxybenzoate, 2,2-di(tert-
butyiperoxy)butane, tert-butyl peroxyacetate, tert-butyl peroxy isopropyl
carbonate, di-tert-butyl peroxide, and 3,3,5,7,7-pentamethyl-1,2,4-
trioxepane.

10. Process according to claim 9 wherein the co-initiator is di-tert-butyl
peroxide or tert-butyl peroxy-3,3,5-trimethylhexanoate.
A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/01 C08F2/34 C08F4/34

According to International Patent Classification (IPC) or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<td>A</td>
<td>EP 1 216 991 Al (AKZO NOBEL NV [NL]) 26 June 2002 (2002-06-26) paragraphs [0018], [0027]; claim 3</td>
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* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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"R" document member of the same patent family

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Further documents are listed in the continuation of Box C.

See patent family annex.
<table>
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