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(54) **Title:** METHOD TO CONTROL MELT ELASTICITY IN LDPE

(57) **Abstract:** Low density polyethylene produced in tubular reactors using free radical initiators in a high pressure process can vary significantly with respect to melt elasticity. Provided is a method for controlling the melt elasticity of low density polyethylene produced in a tubular reactor comprising altering the levels of bi- functional initiator added in multiple injection points relative to the traditional mono- functional initiators added, while striving to maintain desired density and melt index at a preferred conversion rate.

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METHOD TO CONTROL MELT ELASTICITY IN LDPE

TECHNICAL FIELD

The present invention relates to the free radical initiated higher pressure polymerization of ethylene. More specifically, the present invention relates to a process for controlling the melt elasticity of low density polyethylene produced in tubular high pressure reactors by altering the relative levels of mono-functional versus di-functional initiators added at each injection point without significantly altering the peak temperature for each individual injection point.

BACKGROUND ART

Free-radical initiated high pressure polymerization of ethylene was the first process discovered for producing polyethylene, and resulted in a low density polyethylene (LDPE resin) useful for a variety of applications, including film, coating, molding, and cable and wire insulation. Depending on the type of reactor used and the reaction conditions, LDPE resins produced in a free-radical initiated high pressure process can vary widely with respect to polymer properties, particularly those properties that impact processability. Autoclave reactors provide a more dispersed residence time distribution, providing a wide molecular weight distribution indicative of the presence of long chain branching. Conversely, residence times in tubular reactors are more uniform and generally result in a narrower molecular weight distribution. Tubular reactors provide an advantage over autoclave reactors, however, in that they provide higher conversion levels, are more amenable to commercial scale up, and are less capital and energy intensive.

The degree of long chain branching impacts the melt elasticity of a polymer, which can be described as the tendency of a molten polymer to flex or distort. A higher melt elasticity corresponds to a molten polymer that better resists deformation when stretched, which is why LDPE resins with increased levels of long chain branching, and therefore increased melt elasticity, are useful in extrusion coating applications. The resistance to deformation provides reduced neck-in properties suitable for this type of application. Conversely, LDPE resins with reduced long chain branching are more suitable for blown films, which aren't associated with strict neck-in requirements but demand lower haze to be commercially attractive. A process that would allow commercial producers to switch, with minimal process changes, between producing in a tubular reactor, high

and low melt elasticity LDPE resin would be economically advantageous as it would provide a single platform that can be used to produce a selection of LDPE resin polymers that can be used in different applications, differentiated mainly on the degree of long chain branching.

Altering process conditions using a tubular reactor to increase the level of long chain branching is known in the art. U.S. Patent 3,293,233, issued December 20, 1966 in the name of Erchak Jr., et al., assigned to Rexall Drug and Chemical Company, teaches the use of two injection points for introduction of oxygen or a peroxide initiator into a tubular reactor for high pressure production of low density polyethylene. The use of two injection points as opposed to just one corresponded with an increase in the conversion rate and in the long chain branching index, measured as a function of extrudate swelling. The authors also noted that haze improved after adding a second injection point, which conflicts with the notion that increased long chain branching, while increasing melt elasticity, has a detrimental effect on haze. Also, the patent did not teach the use of di-functional initiators, nor the variation of the ratio of di-functional initiators to mono-functional initiators in order to impact the degree of long chain branching. Furthermore, the patent did not address maintenance of peak temperature following each injection point after varying the initiator component. In fact, the effect seen can be attributed to variations in the peak temperature profile seen with the addition of a second injection point.

Long chain branching can be introduced into LDPE resin when produced in a high pressure tubular reactor by using di-functional initiators, as opposed to using the traditional mono-functional initiators that include only a single O-O peroxide bond. A discussion of the mechanism of action for di-functional initiators, which contain at least two O-O bonds, can be found in an article by P.K.F. Khazaeai and R. Dhib in the *Journal of Applied Polymer Science*, Volume 109, pages 3908-3922 (2008). The article teaches that the use of di-functional initiators in high pressure polymerization of ethylene accelerates the polymerization rate, produces branching, and modifies rheological properties. The polymers produced show a much wide molecular weight distribution. The article does not teach the addition of mixture of mono-functional and di-functional initiators into a high pressure process using a tubular reactor with multiple injection points. Furthermore, there is no discussion on how altering the relative levels of the initiators added at each injection point while

maintaining the peak temperature for each injection point can be used to alter the long chain branching without significantly effecting other properties.

U.S. Patent 9,238,700, issued January 19, 2016 in the name of Littmann et al., assigned to Basell Polyolefine GmBH, teaches the use of bi-functional comonomers as a way to incorporate higher levels of long chain branching into LDPE resin. The bi-functional comonomers described contain two different functional groups, including an unsaturated group and a group capable of acting as a chain transfer agent. The bi-functional comonomers are distinct from the initiators used to start the reaction. Also, the patent includes di-functional initiators in its list of possible initiators but does not teach that altering the ratio of di-functional initiator to mono-functional initiator, while maintaining a particular peak temperature profile, can influence the melt elasticity of the resulting LDPE resin.

What is needed is a process where the long chain branching, and ultimately the melt elasticity, can be tailored to suit the desired end use application, while at the same showing little to no variation in other properties, for example melt index and density. Ideally, being able to switch between various types of LDPE resin based primarily on melt elasticity when in possession of a single tubular reactor would give producers an effective tool for producing particular LDPE resins that vary mainly on melt elasticity and can be used in a variety of applications.

SUMMARY OF INVENTION

In one embodiment of the present invention there is provided a process for controlling the melt elasticity of low density polyethylene produced in a free-radical initiated process in a high pressure tubular reactor wherein at least one of one or more mono-functional initiators and one or more di-functional initiators are injected into said tubular reactor via at least one of two or more injection ports at flow rates independently controlled for each mono-functional and di-functional initiator, said process comprising the steps of:

i) raising or lowering the ratio of the flow rate of the one or more di-functional initiators relative to flow rate of the one or more mono-functional initiators injected into said tubular reactor via at least one of said injection ports; and

ii) maintaining the peak temperature control for each of said injection ports, wherein the variation of peak temperature control for each of said injection ports is less than 5%.

In another embodiment of the invention, the alteration of the ratio of the flow rates of the one or more di-functional initiator flow rates relative to the flow rates of the one or more mono-functional initiators injected into said tubular reactor via at least one of said injection ports has no significant effect on the conversion rate, such that the conversion rate varies less than 3%.

In another embodiment of the invention, the alteration of the ratio of the flow rates of the one or more di-functional initiator flow rates relative to the flow rates of the one or more mono-functional initiators injected into said tubular reactor via at least one of said injections ports results in a variation of the melt index of the resulting low density polyethylene that is less than 0.30 dg/10min.

In another embodiment of the invention, the alteration of the ratio of the flow rates of the one or more di-functional initiator flow rates relative to the flow rates of the one or more mono-functional initiators injected into said tubular reactor via at least one of said injection ports results in a variation of the density of the resulting low density polyethylene that is less than 0.005 g/cc.

In another embodiment of the invention the free-radical initiated process further comprises the introduction of a chain transfer agent into said tubular reactor via at least one of said injection ports. The chain transfer agent is selected from the group comprising olefins, aldehydes, ketones, alcohols, saturated hydrocarbons, ethers, thiols, phosphines, amines, amides, esters, and isocyanates, and combinations thereof.

In another embodiment of the invention the chain transfer agent is isopropyl alcohol and is introduced into said tubular reactor at a flow rate from 8 kg/hr to 40 kg/hr, preferably from 20 kg/hr to 38 kg/hr, most preferably from 25 kg/hr to 35 kg/hr.

In another embodiment of the invention the chain transfer agent is heptane and is introduced into said tubular reactor at a flow rate from 8 kg/hr to 40 kg/hr, preferably from 20 kg/hr to 38 kg/hr, most preferably from 25 kg/hr to 35 kg/hr.

In another embodiment of the invention wherein the mono-functional and di-functional initiators are chosen from the group consisting of organic peroxides, hydroperoxides, peresters, and azo compounds.

In an embodiment of the invention at least one of the mono-functional initiators is t-butyl peroxyneodecanoate.

In an embodiment of the invention at least one of the mono-functional initiators is t-butyl peroxy-2-ethylhexanoate.

In another embodiment of the invention at least one of the mono-functional initiators is di-t-butyl peroxide.

In another embodiment of the invention at least one of the di-functional initiators is 1,1-di(t-butylperoxy)cyclohexane.

In an embodiment of the invention the one or more mono-functional initiators are injected into said tubular reactor at a flow rate from 0.1 kg/hr to 10 kg/hr, preferably from 0.15 kg/hr to 8.5 kg/hr, most preferably from 0.2 kg/hr to 7.5 kg/hr.

In an embodiment of the invention said tubular reactor comprises three injection ports.

In another embodiment of the invention said tubular reactor comprises four injection ports.

DESCRIPTION OF EMBODIMENTS

Free-Radical Initiated High Pressure Process

The free-radical initiated high pressure process used for producing low density polyethylene (also referred to herein as LDPE resin) is well known to those skilled in the art. Two types of reactors are used for this process: tubular reactors and autoclave reactors. The present invention is relevant only with respect to tubular reactors. These reactors are characterized by their length, configured in a way that reactants are fed into the reactor at one end and flow through, usually at near steady state, to an output end where LDPE resin is captured. The properties of the LDPE resin produced can vary widely, depending on the flow rates, pressure, temperature, and the types of initiator or initiators used to initiate the polymerization of ethylene. Furthermore, tubular reactors frequently are designed such that initiators can be injected not only at a single injection point located at the front end of the reactor but also at predetermined injection points throughout the length of the reactor. In an embodiment of the invention the tubular reactor comprises a single injection point. In another embodiment the tubular reactor comprises two injection points. In another embodiment of the present invention the tubular reactor comprises three injection points. In yet another embodiment of the present invention the tubular reactor comprises four or more injection points.

The flow rate and pressure used in the process of the present invention may be selected by the person skilled in the art choosing settings appropriate

considering the specific reactor to be used and the desired polymer to be produced. Ranges for both flow rate and pressure would fall within limits normally used and well known in the art.

In an embodiment of the invention mono-functional initiators and di-functional initiators are injected into the tubular reactor via at least one of the injection ports at a flow rates from 0.1 kg/hr to 10 kg/hr, preferably from 0.15 kg/hr to 8.5 kg/hr, most preferably from 0.2 kg/hr to 7.5 kg/hr.

Initiators

In addition to choosing flow rates and pressure a skilled worker must consider the temperature distribution profile along the length of the reactor. In their paper entitled "Free Radical Polymerization Engineering – I. A New Method For Modeling Free Radical Homogeneous Polymerization Reactions", *Chemical Engineering Science*, *39(1)*, 87-99 (1984), Villermaux and Blavier declare that temperature distribution "plays the central role in determining the properties of the polymer products". The free-radical initiated polymerization of ethylene is exothermic, which means that temperature distribution along the length of the reactor is a function of the polymerization reaction and the capacity to remove excess heat. Removing excess heat from tubular reactors is known to those skilled in the art. Known methods are compatible with the present invention.

Choice of initiator or mixture of initiators injected into each injection site will also have an impact on the temperature distribution profile. A large selection of initiators are well known, along with the optimal temperature profile. Choosing an appropriate temperature profile to produce a polymer with desired characteristics is known within the art, and includes the ability to identify initiators that can provide the temperature profile, in combination with the particular reactor and its temperature control abilities. The skilled worker would understand that choosing initiator or initiators one must consider the rate of decomposition and half-life of the initiators.

Mono-functional initiators include compounds having a peroxide functional group, or single O-O bond, having a formula of R_1-OO-R_2. Examples of mono-functional initiators suitable for use with the present invention include organic peroxides, hydroperoxides, peresters, and azo compounds. Specific examples include t-butyl peroxyneodecanoate, t-butyl peroxy-2-ethylhexanoate, and di-t-butyl peroxide.

Di-functional initiators include compounds that include two peroxide functional groups having a formula of R_1-OO-R_2-OO-R_3. Examples of di-functional initiators suitable for use with the present invention include organic peroxides, hydroperoxides, peresters, and azo compounds. In an embodiment of the present invention the di-functional initiator is 1,1-di-(t-butylperoxy)cyclohexane.

Chain Transfer Agents

Another common addition to tubular reactors during free-radical initiated polymerization of ethylene are chain transfer agents. During propagation the free-radical at the end of the growing chain is transferred to the newly added ethylene molecule providing a reactive end for addition of the next ethylene molecule. Propagation can continue provided the final ethylene retains the free radical. Chain transfer agents allow termination of the growing chain by transferring the free radical to the chain transfer agent, without reforming a free radical at the end of the growing polyethylene chain. The chain transfer agent having a free radical is now a target for propagation through addition of ethylene monomers. Chain transfer agents in effect control the length or average molecular weight of the polyethylene produced. Without a chain transfer agent the molecular weight is normally controlled by altering reaction conditions.

Chain transfer agents commonly used in the art include olefins, aldehydes, ketones, alcohols, saturated hydrocarbons, ethers, thiols, phosphines, amines, amides, esters, and isocyanates, and combinations thereof. Any of these are appropriate for use with an embodiment of the present invention.

In embodiment of the present invention the chain transfer agent is isopropyl alcohol. In yet another embodiment of the invention the chain transfer agent is heptane.

Flow rates of chain transfer agent used also fall within the scope of knowledge possessed by the skilled person. The rate may vary between injection points when a reactor with more than one injection point is used.

In an embodiment of the present invention the chain transfer agent introduced into the reactor via at least one of the injection ports is injected at a flow rate from 8 kg/hr to 40 kg/hr, preferably from 20 kg/hr to 38 kg/hr, most preferably from 25 kg/hr to 35 kg/hr.

Peak Temperature

The temperature distribution profile refers to the temperature within and along the length of the reactor. Ethylene entering the reactor at the inlet is preheated so as to promote decomposition of the free-radical initiator, forming free-radicals that can start polymerization. The preheat temperature is chosen to align with the decomposition temperature of the initiator or initiators injected into the reactor at the upstream end. The peak temperature within the reactor at the upstream end and following initiator injection points is a function of the quantity of initiator injected into the reactor. The temperature peaks at a point where the initiator levels drop off and polymerization reduces due to lower levels of free-radicals. The release of heat by polymerization increases the temperature within the reactor, an effect that can be partially minimized by cooling means in the form of a water cooled jacket surrounding the reactor. Increasing the quantity of initiator at any point has the effect of increasing the peak temperature. Conversely, decreasing the amount of initiator lowers the peak temperature.

The temperature within and along the length of the reactor can be plotted versus position along the length of the reactor to give a temperature distribution profile. The peak temperatures for each injection point are clearly seen in the profile as the temperature peaks immediately downstream of each injection point, then gradually cools before the next injection point or at the end of the reactor. The experienced operator understands that the temperature distribution profile can be associated with various properties found in the LDPE resin produced. Alteration of the profile by altering peak temperature of one or more of the injection points can have effects on the molecular structure and hence the properties of the resulting polymer. Furthermore, changing the peak temperatures may also impact the conversion rate of ethylene, or ethylene and one or more comonomers, into polyethylene. For the present invention the peak temperature for each injection point may vary.

Melt Elasticity

The present invention seeks to provide a way of altering the melt elasticity of a low density polyethylene produced in a free-radical initiated process. The present invention is useful for modifying melt elasticity while attempting to maintain other properties of the LDPE resin as to provide consistency among produced resins.

The process seeks to provide a way to produce resins that differ mainly in their degree of long chain branching.

Melt elasticity can be assessed in a number of ways, including the use of rheological measurements. For the purposes of the present invention melt elasticity is quantified by G' at G" = 500 kPa. The higher the G' at G" = 500 kPa the higher the melt elasticity. The melt elasticity is dependent upon the degree of long chain branching within the polymer. Long chain branching is commonly present in LDPE resin produced in a free-radical initiated high pressure process, but the levels are enhanced when di-functional initiators are used in the process.

The present invention begins with an LDPE resin that satisfies particular properties with the exception of melt elasticity, and acts to alter the process conditions to produce a similar LDPE resin but with an altered melt elasticity. For example, an operator may be using process conditions that result in an LDPE resin within a desired density range, but not with the required melt elasticity. In that instance the present invention may provide a solution that increases melt elasticity but does significantly alter density. In an embodiment of the invention the peak temperature for each injection point does not vary by more than 5°C.

The change in the ratio of di-functional initiator to mono-functional initiator is performed with the melt elasticity in mind. For a higher melt elasticity, an increase in the amount of di-functional initiator added to at least one of the injection points is required. In order to prevent a significant change in the peak temperature a corresponding decrease in the mono-functional initiators at the same injection point would be required. The present invention also contemplates adding di-functional initiator to one or more injection points where previously no di-functional initiator was added. As before, the skilled operator would understand that in that instance the amount of mono-functional initiator added at the same injection point would need to be reduced to keep the peak temperature within a desired range.

Applications that would benefit from the present invention include producing resins for foaming and extrusion coating applications. In that instance the ratio of di-functional initiator to mono-functional initiator would be increased for at least one of the injection points. The greater the desired increase in melt elasticity means allowing for a greater the change in the ratio or for increasing the number of injection points where the ratio is increased.

Applications where reducing the melt elasticity is desired include film applications. In film, a lower haze is desirable because it provides more clarity. In a process where LDPE resin with higher melt elasticity is produced, the operator may reduce the ratio of di-functional initiator to mono-functional initiator added to one or more of the injection points. In order to maintain the peak temperature an alteration in the amount of mono-functional initiator, or chain transfer agent, added would be required. In addition, the present invention contemplates removing di-functional initiators entirely so as to reduce the melt elasticity to its lowest possible in the prevailing conditions, including the temperature distribution profile. By maintaining the temperature profile the production or conversion rate is not significantly lowered, an effect that would be expected when di-functional initiators are removed from the process.

EXAMPLES

Four experimental LDPE resins were produced in a tubular reactor with four injection points. The peak temperature controls for each injection point, which determine the temperature distribution profile, are shown in Table 1. Resins A through C share a similar temperature distribution profile, with peak temperature control at each injection not varying by more than 2°C. The fourth resin, a comparative, used a unique temperature distribution profile where peak temperature control for all four injection points were higher than those used for the experimental resins A through C.

TABLE 1

Peak Temperature Control for Each Injection Point Values are in °C

	Comp.	Resin A	Resin B	Resin C
1st injection point	267	255	254	252
2nd injection point	267	250	250	249
3rd Injection point	266	240	240	239
4th Injection point	267	238	241	239

Table 2 lists the flow rates of initiators and chain transfer agents added at each injection point for the resins produced. The mono-functional initiators employed include t-butyl peroxyneodecanoate (MFI-1), t-butyl peroxy-2-ethylhexanoate (MFI-2), and di-t-butyl peroxide (MFI-3). The di-functional initiator employed was 1,1-di-(t-butylperoxy)cyclohexane (DFI-1) and the chain transfer

agent employed was isopropyl alcohol (IPA). The sample resins A through C differed in the flow rates for the di-functional initiator (DTBC) added at the 2nd and 3rd injection points. In resin A the flow rate for DTBC at the 2nd injection point was doubled, and at the 3rd injection point DTBC was included whereas it was absent for resins B and C. Additionally, to maintain peak control temperature Resin A was produced without the use of the mono-functional initiator DTBP. The comparative resin employed a unique combination of initiators, maintaining a higher peak control temperature for each of the injection points mainly due to higher flow rates for the DTBP mono-functional initiator.

TABLE 2

Flow Rates (Kg/Hr) of Mono-Functional and Di-Functional Initiators, and Chain Transfer Agent Added at Each Injection Point

	Comp.	Resin A	Resin B	Resin C
1st Injection Point				
MFI-1	5.00	7.00	7.00	7.00
MFI-2	4.00	4.00	4.00	4.00
MFI-3	0.28	0.00	0.05	0.04
DFI-1	0.66	0.49	0.25	0.24
IPA	21.00	24.02	20.00	20.00
2nd Injection Point				
MFI-1	5.50	7.00	5.50	5.50
MFI-2	4.50	6.00	4.50	4.50
MFI-3	1.04	0.00	0.34	0.37
DFI-1	2.00	4.10	2.00	2.00
IPA	20.01	21.03	20.01	20.01
3rd Injection Point				
MFI-1	0.00	0.00	0.00	0.00
MFI-2	0.01	2.70	3.00	3.00
MFI-3	1.40	0.00	0.15	0.16
DFI-1	1.00	2.00	0.00	0.00
IPA	19.00	20.00	19.99	20.01
4th Injection Point				
MFI-1	0.00	0.00	0.00	0.00
MFI-2	0.00	4.00	0.00	0.00
MFI-3	0.983	0.00	0.251	0.227
DFI-1	0.00	0.00	0.00	0.00
IPA	13.99	16.04	15.99	15.00

The properties of the resins produced demonstrate the usefulness of the present invention. By increasing the amount of di-functional initiator added at one or more of the injection points a change in the melt elasticity, measured as G' @ G" = 500 kPa, was seen. The change in melt elasticity did not result in a significant change in the density, MI, or polydispersity index (PDI). By maintaining a temperature distribution profile, through non-variance of peak temperature control at each injection point, the melt elasticity of an free-radical initiated LDPE resin can be manipulated by changing the amount of di-functional to mono-functional initiator added at one or more of the injection points. Resin A comprises the highest G' value and would suitable for use in foaming type applications. Resins B and C comprise lower G' values but are improved in their haze %, making them suitable for use in film applications. These results show that when starting with a particular resin, for example Resin B, the amount of initiators added may be altered while keep the peak temperature control consistent to produce a resin that varies mostly in respect to the G' value.

TABLE 3

Product Properties

	Comp.	Resin A	Resin B	Resin C
MI (dg/min)	2.37	2.30	2.28	2.00
Density (g/cc)	0.9212	0.9234	0.9237	0.9235
G' @ G"=500kPa (kPa)	73.00	80.00	73.00	77.00
Mn (g/mol)	20028	20931	23123	21277
Mw (g/mol)	65820	61509	64513	61652
Mz (g/mol)	144951	129110	131169	1206636
PDI	3.29	2.90	2.79	2.90
Haze (%)	5.10	5.20	4.50	4.80

INDUSTRIAL APPLICABILITY

The method described is applicable for altering melt properties of low density polyethylene. The method is useful for making low density films and for foaming and extrusion coating applications.

CLAIMS

1. A process for controlling melt elasticity of low density polyethylene produced in a free-radical initiated process in a high pressure tubular reactor wherein at least one or more mono-functional initiators and one or more di-functional initiators are injected into said tubular reactor via at least one of two or more injection ports at flow rates independently controlled for each mono-functional and di-functional initiator, wherein said process comprises the steps of:

i) raising or lowering the ratio of the flow rate of the one or more di-functional initiators relative to flow rate of the one or more mono-functional initiators injected into said tubular reactor via at least one of said injection ports; and

ii) maintaining the peak temperature control for each of said injection ports, wherein the variation of peak temperature control for each of said injection ports is less than 5°C; and

wherein melt elasticity is increased when said ratio is increased and melt elasticity is decreased when said ratio is lowered.

2. The process according to claim 1 further comprising maintaining the conversion rate of ethylene into polyethylene, wherein the variation of conversion rate of ethylene into polyethylene is less than 3%.

3. The process according to claim 1 further comprising maintaining the melt index of the resulting low density polyethylene, wherein the variation of the melt index is less than 0.30 dg/10min.

4. The process according to claim 1 further comprising maintaining the density of the resulting low density polyethylene, wherein the variation of the density is less than 0.001 g/cc.

5. The process according to any of the preceding claims where in the free radical initiated process further comprises injecting a chain transfer agent into said tubular reactor via at least one or more of said injection ports.

6. The process according to claim 6, wherein the chain transfer agent is selected from the group consisting of olefins, aldehydes, ketones, alcohols, saturated hydrocarbons, ethers, thiols, phosphines, amines, amides, esters, and isocyanates, and combinations thereof.

7. The process according to claim 6, wherein the chain transfer agent is isopropyl alcohol.

8. The process according to claim 8, wherein the chain transfer agent is isopropyl alcohol, and the isopropyl alcohol is introduced to the reactor into each of the injection ports at a flow rate from 8 kg/hr to 40 kg/hr, preferably from 20 kg/hr to 38 kg/hr, most preferably from 25 kg/hr to 35 kg/hr.

9. The process according to claim 6, wherein the chain transfer agent is heptane.

10. The process according to claim 10, wherein the chain transfer agent is heptane, and the heptane is fed to the reactor into each of the injection ports at a flow rate from 8 kg/hr to 40 kg/hr, preferably from 20 kg/hr to 38 kg/hr, most preferably from 25 kg/hr to 35 kg/hr.

11. The process according to any of the preceding claims, wherein the mono-functional and di-functional initiators are selected from the group consisting of organic peroxides, hydroperoxides, peresters, and azo compounds.

12. The process according to claim 12, wherein at least one of the mono-functional initiators is t-butyl peroxyneodecanoate.

13. The process according to claim 12, wherein at least one of the mono-functional initiators is t-butyl peroxy-2-ethylhexanoate.

14. The process according to claim 12, wherein at least one of the mono-functional initiators is di-t-butyl peroxide.

15. The process according to claim 12, wherein at least one of the di-functional initiators is 1,1-di-(t-butylperoxy)cyclohexane.

16. The process according to any of the preceding claims, wherein each mono-functional initiator is injected into at least one of the injection ports at a flow rate from 0.1 kg/hr to 10 kg/hr, preferably from 0.15 kg/hr to 8.5 kg/hr, most preferably from 0.2 kg/hr to 7.5 kg/hr.

17. The process according to claim 1, wherein said reactor comprises three injection ports.

18. The process according to claim 1, wherein said reactor comprises four injection ports.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/01 C08F2/34
ADD.

According to International Patent Classification (IPC) or to 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/295289 A1 (LITTMANN DIETER [DE] ET AL) 7 November 2013 (2013-11-07) the whole document	1-18
A	WO 2008/112373 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; AERTS PETER [NL]; BERBEE OTTO [NL]) 18 September 2008 (2008-09-18) the whole document	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* 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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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2018	28/05/2018

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2018/051484

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