Title: METHOD FOR PREPARING ETHYLENE COPOLYMER

Abstract: The invention provides a process for preparing an ethylene copolymer by copolymerizing ethylene and at least one comonomer at pressures in the range of from 150 MPa to 350 MPa and temperatures in the range of from 50°C to 350°C by: (i) a process in the presence of a system initially consisting of an initiator having a radically transferable atom and a catalyst of a transition metal complex or (ii) a process in the presence of a system initially consisting of an initiator having a radically transferable atom, a catalyst of a transition metal complex and a reducing agent, wherein the amount of the at least one comonomer in the ethylene copolymer is 0.05-65 mol%.
Method for preparing ethylene copolymer

The invention relates to a process for preparing an ethylene copolymer. The invention further relates to such ethylene copolymer obtainable by the process.

Known processes for making polyethylene and its copolymers include random polymerization. US4177340A discloses a high pressure free radical polymerization of ethylene with oxygen as initiator and 0.01-0.5% weight of an alkyl ester or alkenemonocarboxilic acid ester, in this case butyl acrylate. Final polymer contains about 0.2% by weight of n-butyl acrylate incorporated.

US2012035323 (A1) mentions commercially available unfunctionalized acrylate copolymers, which are made by high pressure random polymerization. These copolymers generally comprise a major portion by weight of an olefin monomer, usually ethylene, and a minor portion, typically up to about 30% by weight, of an acrylic monomer, usually methyl acrylate or butyl acrylate.

Ethylene vinyl acetate copolymers made by high pressure random polymerization are also known. Examples of commercially available EVA copolymers generally comprise 9-42 wt% of vinyl acetate.

Macromol. Chem. Phys. 2001, 202, No 7, Buback et. al., High-Pressure Free Radical Copolymerization of ethene and methyl methacrylate, refers to free radical high pressure Copolymerization of ethylene and butyl methacrylate with incorporation up to 45% mol BMA.

Atom transfer radical polymerization (ATRP) is well-known and described in detail in many publications. For example, US2011/0082230 gives a detailed description of the ATRP technique and some of its improved techniques, such as ICAR (Initiators for Continuous Activator Regeneration) ATRP and ARGET (Activator ReGenerated by Electron Transfer) ATRP.

ATRP has been applied in the homopolymerization of acrylates at high pressure as well as in the copolymerization of (meth)acrylates and small percentages of α-olefins under normal reaction conditions. For example, EP1171496 discloses the
(co)polymerization of (meth)acrylates using ATRP. EP1171496 discloses preparation of methyl methacrylate grafted polyethylene by ATRP (Example 37e). In this process, the location of the methyl methacrylate block is limited to the side branches and the amount of methyl methacrylate incorporated in the polyethylene backbone is limited.

Macromolecular rapid communications, 2013, 34, 604-609, Wang et. al describes high pressure Atom Transfer Radical Polymerization (ATRP) of n-butyl acrylate.

Known processes for preparing an ethylene copolymer have the disadvantage that a limited amount of comonomers is incorporated in the final ethylene copolymer.

It is an object of the invention to provide a process for preparing an ethylene copolymer in which above-described and/or other problems are solved.

Accordingly, the invention provides a process for preparing an ethylene copolymer by copolymerizing ethylene and at least one comonomer at pressures in the range of from 150 MPa to 350 MPa and temperatures in the range of from 50°C to 350°C by:

(i) a process in the presence of a system initially consisting of an initiator having a radically transferable atom and a catalyst of a transition metal complex or

(ii) a process in the presence of a system initially consisting of an initiator having a radically transferable atom, a catalyst of a transition metal complex and a reducing agent,

wherein the amount of the at least one comonomer in the ethylene copolymer is 0.05-65 mol%.

Advantageously, the process according to the invention allows the incorporation of a high amount of the comonomer in the polyethylene backbone. At similar comonomer concentrations in the feed, the process according to the invention results in ethylene copolymers with a higher amount of incorporated comonomer compared to known processes.

Further advantages of the process according to the invention may include that the process according to the invention results in an ethylene copolymer with a narrow molecular weight distribution (lower polydispersity index (PDI).)

The term "ethylene copolymer" is herein understood as a copolymer in which at least
35 mol% of the copolymer is ethylene. Accordingly, the invention is a process for preparing an ethylene copolymer by copolymerizing ethylene and at least one comonomer at pressures in the range of from 150 MPa to 350 MPa and temperatures in the range of from 50°C to 350°C by:

(i) a process in the presence of a system initially consisting of an initiator having a radically transferable atom and a catalyst of a transition metal complex or
(ii) a process in the presence of a system initially consisting of an initiator having a radically transferable atom, a catalyst of a transition metal complex and a reducing agent,

wherein the amount of the at least one comonomer in the ethylene copolymer is 0.05-65 mol% and the amount of ethylene in the ethylene copolymer is 35-99.95 mol%.

The process (i) is generally known as ATRP process. The process (ii) is generally known as an ICAR ATRP process or an ARGET ATRP process, depending on the type of the reducing agent. All of these processes are well known.

For the description of ATRP, ICAR ATRP and ARGET ATRP, US2011/0082230 is referred and incorporated herein by reference. ATRP, ICAR ATRP and ARGET ATRP are described below based on US2011/0082230 as follows.

The term "ATRP" is herein understood to mean the 'classical' ATRP process described generally by scheme 1.

\[
P_n + X + M^{n+1}_{t}/\text{Ligand} \xrightarrow{k_a} P_n^* + X + M^{n+1}_{t}/\text{Ligand} \xrightarrow{k_p} P_n \xrightarrow{k_d} P_m
\]

Scheme 1. General mechanism of ATRP

A typical ATRP process comprises the use of a transition metal complex in its lower oxidation state that acts as a catalyst for the controlled polymerization of radically (co)polymerizable monomers and an initiator possessing one or more transferable atoms which are typically halogen (ATRP initiator).

Suitable ATRP initiators are substituted alkyl halides attached to a low molecular
weight molecule with an additional non-initiating functionality, a low molecular weight initiator or macroinitiator with two or more transferable atoms.

The ATRP initiator \((P_nX, n=0\) in scheme 1) or dormant polymer \((n>1,\) in that case called macroinitiator) and the lower oxidation state transition metal catalyst take part in a redox reaction continuously in which the lower oxidation state transition metal catalyst \((M^{n+}/\text{Ligand in scheme 1})\) induces the homolytic cleavage of the \(Pn-X\) bond of the ATRP initiator or dormant polymer chain removing therefore a transferable atom \((X=\) typically halogen) to form an active radical \((P_n^\cdot)\) at a rate of reaction \(k_a.\) The reverse reaction \((k_{da}).\) in which the higher oxidation state transition metal catalyst \((X-M^{n+}/\text{Ligand})\) deactivates these radicals by donating back a transferable atom proceeds at a faster rate so that the radical concentration is lowered and these active species have only short time to propagate \((k_p) / \) terminate \((k_t)\) before they are trapped into the dormant state \((P_nX).\)

Importantly, the catalyst is not bound to the polymer chains, as in coordination polymerization, and can therefore be used in a controlled/living polymerization process at sub-stoichiometric amounts relative to the initiator.

Modifications of the ATRP technique in terms of amount of catalyst used are for instance ARGET ATRP and ICAR ATRP, generally described by scheme 2, using Cu as transition metal.

\[
\begin{align*}
R &\rightleftharpoons X + Cu^I \overset{k_d}{\rightleftharpoons} X/Ligand \\
&\underset{k_{da}}{\rightleftharpoons} +M \overset{k_p}{\rightarrow} \overset{k_t}{\rightarrow} R' \\
\therefore R &\rightarrow R + Cu^{II} \overset{k_I}{\rightarrow} X_2/Ligand
\end{align*}
\]

Scheme 2. ATRP modified techniques
The amounts of the catalyst used for the ARGET ATRP and the ICAR ATRP can be reduced from for example 10,000 ppm with respect to the monomers to 1-100 ppm with respect to the monomers by addition of a reducing agent that acts throughout the polymerization continuously regenerating the lower oxidation state transition metal catalyst (Mⁿ⁻¹/Ligand) from accumulating higher oxidation state transition metal catalyst (X-Mⁿ⁺/Ligand).

In Scheme 2, when the regeneration is conducted by addition of a reducing agent which does not take part in radical reactions, the technique is called activators regenerating by electron transfer (ARGET ATRP). In case that such reducing agent is a free radical initiator which additionally participates in the polymerization as an extra source of radicals, the process is called Initiators for Continuous Activator Regeneration Atom Transfer Radical Polymerization (ICAR ATRP).

process (i): ATRP

The copolymerization in the process according to the invention may be performed by process (i) (ATRP). The process (i) is performed in the presence of a system initially consisting of an initiator having a radically transferable atom and a catalyst of a transition metal complex. The radically transferable atom is typically a halogen.

Suitable examples of the initiators having a radically transferable atom include compounds represented by formulas R¹R²R³C-X, R¹-(CO)-X, R¹R²R³Si-X or R¹R²N-X or R¹NX₂ whereby

X is selected from the group consisting of Cl, Br and I;
R¹, R² and R³ are each independently selected from the group consisting of H, halogen, C₁⁻C₂₀ linear or branched alkyl, C₂⁻C₈ cycloalkyl, COCl, COBr, OH, CN, C₂⁻C₂₀ alkenyl or alkynyl, oxiranyl, glycidyl, C₂⁻C₆ alkylenec or alkenylene substituted with oxiranyl or glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl and COO-R⁴ wherein R⁴ is selected from the group consisting of C₁⁻C₂₀ linear or branched alkyl, C₂⁻C₆ alkenyl, C₂⁻C₆ alkynyl, N-hydroxysuccinimide, poly(ethylene glycol) methyl ether, C₁⁻C₂₀ alkyl substituted with e.g. an azide, methacrylate, alcohol, phthalimido or 2,2-dimethyl-1,3-dioxolan-4-yl.

Particularly preferred examples of the initiators include methyl-2- bromopropionate (R¹R²R³C-X wherein X=Br, R¹=H, R²=CH₃, R³=COOR⁴ wherein R⁴=CH₃).
Further suitable initiators include multifunctional initiators such as bis[2-(2'-bromoiso- 
butyl]oxyethyl]disulfide, bis[2-(2-bromoiso- 
butyl]oxy]undecyl] disulfide, 2- 
bromoiso- 
butyric anhydride, dipentaerythritol hexakis(2-bromoiso- 
butyrate), ethylene 
bis(2-bromoiso- 
butyrate), pentaerythritol tetrakis(2-bromoiso- 
butyrate), poly(ethylene 
glycol) bis(2-bromoiso- 
butyrate), 1,1,1-tris(2-bromoiso- 
butyloxymethyl)ethane.

The transition metal complex comprises a transition metal salt and a ligand.
Suitable examples of the transition metal salt include compounds represented by 
formula $M^{n+}Y_n$

wherein
$M^{n+}$ is selected from the group consisting of Cu$^{1+}$, Cu$^{2+}$, Co$^{3+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Mo$^{4+}$, Mo$^{5+}$, 
Mo$^{2+}$, Mo$^{3+}$, Mo$^{5+}$, Ni$^{2+}$, Ni$^{3+}$, Ni$^{4+}$, Ru$^{2+}$, Ru$^{3+}$, Ru$^{4+}$, Ru$^{5+}$, Ru$^{6+}$, Ti$^{3+}$, Ti$^{4+}$, Ag$^{+}$, Ag$^{2+}$, Pd$^{0}$, 
Pd$^{2+}$, Pd$^{2+}$, Pt$^{0}$, Pt$^{2+}$, Pt$^{3+}$, Pt$^{4+}$, Zn$^{+}$ and Zn$^{2+}$.

$Y$ is selected from the group consisting of halogen, OH, (O)$_{1/2}$, CN, NC, SCN, CNS, 
OCN, CNO, N$_5$ and R$^5$CO$_2$ where R$^5$ is selected from H, linear or branched alkyl or 
aryl which may optionally be substituted with one or more halogens and 
n is the formal charge on the metal.

Particularly preferred examples of the transition metal complex include CuBr.

Suitable examples of the ligands which can be used in combination with above 
mentioned transition metal salts include 
pyridines such as N-butyl-2-pyridylmethamine, N-dodecyl-N-(2-
pyridylmethylene)amine, N-octadecyl-N-(2-pyridylmethylene)amine and N-octyl-2-
pyridylmethamine,
bipyridines such as 2,2'-bipyridyl, 4,4'-di-tert-butyl-2,2'-dipyridyl, 4,4'-dimethyl-2,2'-
dipyridyl and 4,4'-inoxy-2,2'-dipyridyl,
bipyrole and derivatives thereof,

acetonitrile,
1,10-phenanthroline,
porphyrin and derivatives thereof,
porphycene and derivatives thereof,
crown ethers such as 18-crown-6,
cyclopentadienyl and derivatives thereof,
benzene and derivatives thereof,
amines such as ethylenediamine, propylenediamine, 1,1,4,7,10,10-
hexamethyltriethylenetramine, N,N,N',N",N"'-pentamethylbienethylenetriamine, 1,4,8,11-
tetraazacyclotetradecane, N,N,N',N"'-tetrakis(2-pyridylmethyl)ethylenediamine, 1,4,8,11-
tetramethyl-1,4,8,11-tetraazacyclotetradecane, tris[2-(dimethylamino)ethyl]amine,
tris(2-pyridylmethyl)amine,
aminoethanol and aminopropanal (both optionally substituted one to three times on the
oxygen and/or nitrogen atom with a C_1-C_4 alkyl group),
ethylene glycol and propylene glycol (both optionally substituted one to two times on
the oxygen atoms with a C_1-C_4 alkyl group) and
carbon monoxide.

Particularly preferred examples of the ligand include tris(2-pyridylmethyl)amine.

Preferably, the amount of the initiator may be 10-1000 molppm with respect to the total
of the ethylene and the at least one comonomer to be copolymerized.

Preferably, the amount of the transition metal salt is 5000-10000 molppm with respect
to the total of the ethylene and the at least one comonomer to be copolymerized.

Preferably, the amount of the ligand is used in excess respect to the transition metal
salt in order to ensure the formation of transition metal complex.

**process (ii): ICAR and ARGET ATRP**

Preferably, the copolymerization in the process according to the invention is performed
by process (ii) (ICAR ATRP or ARGET ATRP). The process (ii) is performed in the
presence of a system initially consisting of an initiator having a radically transferable
atom, a catalyst of a transition metal complex and a reducing agent.

Suitable examples of the initiator, transition metal salt and ligand suitable for process
(ii) include the initiator, transition metal salt and ligand described with respect to
process (i). The transition metal complex is in its high oxidation state.

When the reducing agent is a free radical initiator which additionally participates in the
polymerization as an extra source of radicals, the process is ICAR ATRP. The free
radical initiator may be any molecule that may be induced to form free radicals, such as
a molecule that forms radicals by thermal, photoiniated or other decomposition
processes. Free radical initiators include peroxides, azo compounds, disulfides, and tetrazines. More specifically, free radical initiators include acyl peroxides, benzoyl peroxides, alkyl peroxides, cumyl peroxides, tributyl peroxides, hydroperoxides, cumyl hydroperoxide, tert-butyl hydroperoxide, peresters, tert-butyl perbenzoate, alkyl sulfonyl peroxides, dialkyl peroxydicarbonates, diperoxyketals, ketone peroxides, 2,2'-azobisisobutyronitrile (‘AlBN’), 2,2'-azobis(2,4-dimethyl pantenonitrile), and 1,1'-azobis (cyclohexane-carbonitrile).

When the reducing agent does not act as an extra source of radicals, the process is ARGET ATRP. Such reducing agent may be an organic compound selected from the group consisting of alkylthiols, mercaptoethanol, enolizable carbonyl compounds, ascorbic acid, acetyl acetone, camphorsulfonic acid, hydroxy acetone, reducing sugars, monosaccharides, glucose, hydrazine, aldehydes, and derivates of any thereof. Other examples of such reducing agent are Cu(I) and tin(II) 2-ethylhexanoate.

The amounts of the initiator having a radically transferable atom or group, the transition metal salt and the ligand may be easily selected by the skilled person depending on the desired product properties. For example, the amount of the initiator having a radically transferable atom or group is 10-300 molppm with respect to the total of the ethylene and the at least one comonomer to be copolymerized.

Preferably, the amount of the initiator having a radically transferable atom may be 10-1000 molppm with respect to the total of the ethylene and the at least one comonomer to be copolymerized.

Preferably, the amount of the transition metal salt is 10-200 molppm with respect to the total of the ethylene and the at least one comonomer to be copolymerized.

Preferably, the amount of the ligand is in excess respect to the transition metal salt to ensure the formation of the transition metal complex.

In the cases where the reducing agent is a free radical initiator, the molar ratio of the reducing agent which is the free radical initiator with respect to the initiator having a radically transferable atom is preferably 0.01-0.5, more preferably 0.01-0.1.

In the cases where the reducing agent does not act as an extra source of radicals, the
amount of the reducing agent is preferably 10-1000 molppm with respect to the total of
the ethylene and the at least one comonomer to be copolymerized.

high pressure polymerisation process

The high pressure polymerisation process of ethylene is disclosed e.g. by Andrew
Peacock (Handbook of Polyethylene. Marcel Dekker, Inc. ISBN: 0-8247-9546-6; 2000),
in particular, at pages 43-66. Peacock describes the free radical chemical processes,
the high pressure production facilities and the high pressure reaction conditions.

The high pressure reactors for the ethylene copolymer can take one of two forms being
either an autoclave, with a height-to-diameter ratio in the region of 2-20, or a tubular
reactor, with a length-to-diameter ratio from a few hundred up to tens of thousands.
These two divergent reactor geometries pose uniquely different chemical engineering
problems requiring disparate control conditions. Tubular and autoclave reactors with
their disparate profiles require different methods of temperature control.

The autoclave process and the tubular process result in different chain architecture
(Tackx and Tack, Polymer Volume 39, number 14, pp 3109-3113, 1998) and different
molecular weight distribution of the polymer (Kaltenbacher et al, Vol 50, No 1, January
1967, TAPPI).

The process of the invention is carried out at pressures of from 150 MPa to 350 MPa.
The pressures may preferably be 160 MPa to 300 MPa or more preferably 160 MPa to
280 MPa. The temperatures are in the range from 50°C to 350°C, preferably from 60°C
to 300°C, for example 65 °C to 250 °C, for example 70 °C to 200 °C, for example 75 °C
to 150 °C, for example 80 °C to 100 °C.

It is important that the compounds present in the copolymerization process do not
undergo degradation during the copolymerization. The temperature and pressure
should be chosen to ensure that degradation does not occur. High pressure Differential
Thermal Analysis (DTA) may be carried out on the compounds present in the
copolymerization process for determining its thermal stability to choose the
temperature and pressure for the copolymerization. For example, the temperature is
preferably below 220 °C when the initiator having a radically transferable atom is
methyl-2-bromopropionate.
Examples of suitable comonomers for use in the process of the present invention include \( \alpha,\beta \)-unsaturated \( C_2-C_8 \)-carboxylic acids, in particular maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid and crotonic acid; derivatives of \( \alpha,\beta \)-unsaturated \( C_3-C_8 \)-carboxylic acids, e.g. unsaturated \( C_3-C_{15} \)-carboxylic esters, in particular esters of \( C_1-C_6 \)-alkanols, in particular methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, or anhydrides, in particular methacrylic anhydride, maleic anhydride or itaconic anhydride;

1-olefins such as propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonenone or 1-decene;
cyclic olefins such as cyclobutene, cyclopentene, cyclohexene, cycloheptene and cyclooctene, cyclooctadiene, cyclononene, cyclodecene, 1-methyl-1-cyclohexene, 3-methyl cyclohexene, alpha-pinene or norbornene.

Vinyl monomers such as vinyl carboxylates, particularly preferably vinyl acetate, or styrene can be used as comonomers.

Preferably, the at least one comonomer is selected from the group consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate and tert-butyl acrylate.

Suitable comonomers for use in the process of the present invention further include bifunctional comonomers. Examples of suitable bifunctional comonomers for use in the process of the present invention are 1,4-butanediol dimethacrylate, hexanediol dimethacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, dodecanediol dimethacrylate, glycerol dimethacrylate, 1,4-butanediol diacylate, hexanediol diacylate, ethylene glycol diacylate, 1,3-butylene glycol diacylate, dodecanediol diacylate, glycerol diacylate, poly(ethylene glycol) dimethacrylate, poly(propylene glycol) dimethacrylate, poly(ethylene propylene glycol) dimethacrylate, 1,4-butanediol divinyl ether, poly(ethylene glycol) divinyl ether, di(ethylene glycol) divinyl ether, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene and 1,13-tetradecadiene.

The amount of the at least one comonomer in the ethylene copolymer is 0.05-65 mol%, for example at least 1 mol%, at least 5 mol%, at least 10 mol%, at least 15 mol%, and/or at most 60 mol%, at most 50 mol%, at most 40 mol% or at most 30 mol%. 
Preferably, the amount of the at least one comonomer with respect to the total of the ethylene and the at least one comonomer to be copolymerized is 0.001-10 mol%, for example at least 0.1 mol%, at least 1 mol% or at least 2 mol% and/or at most 7.5 mol% or at most 5 mol%.

Preferably, the ethylene copolymer according to the present invention has a density of 900 to 1100 kg/m³ for example 905 to 1000 kg/m³, 910 to 990 kg/m³, 915 to 970 kg/m³ or 918 to 960 kg/m³, 920 to 950 kg/m³, according to ISO1183.

Preferably, the ethylene copolymer according to the present invention has a melt flow rate of 0.10 g/10 min to 150 g/10 min according to ASTMD1238 measured at 190 °C and 2.16 kg. Preferably, the ethylene copolymer according to the present invention has a melt flow rate of 10 to 900 g/10min according to ASTMD1238 measured at 125°C and 0.325kg.

The process of the present invention can be carried out with all types of tubular reactors suitable for high-pressure polymerization.

Preferably the comonomer is first mixed with ethylene before it is brought into contact with the system comprising the initiator. It is possible to feed such a mixture of ethylene and the comonomer only to the inlet of the tubular reactor. It is also possible to feed more than one stream of ethylene and the comonomer and feed accordingly one or more of these streams as side stream to the tubular reactor.

The process of the present invention can also be carried out with all types of autoclave reactor. Such reactors generally have height to diameter ratios from 1 up to 20. Residence time may generally be between 8 up to 120 s.

The process of the present invention can be carried out in a single tubular reactor or a single autoclave reactor. The process of the present invention can also be carried out in 2 or more tubular reactors connected in series, 2 or more autoclave reactors connected in series or an autoclave reactor and a tubular reactor connected in series. Such a process for producing polymers or copolymers of ethylene using an autoclave reactor and a tubular reactor connected in series is known e.g. from US4496698.

The invention further relates to an ethylene copolymer obtainable by the process of the
invention.

Preferably, the ethylene copolymer according to the invention has $M_w$ of at least 10 kg/mol, for example at least 20 kg/mol, at least 30 kg/mol or at least 40 kg/mol. Typically, the ethylene copolymer has $M_w$ of at most 500 kg/mol, for example at most 450 kg/mol, according to gel permeation chromatography. $M_n$ and $M_w$ may be determined by gel permeation chromatography, e.g. by the methods described in the experimental section.

Preferably, the ethylene copolymer according to the invention has a polydispersity index (PDI=$M_w$/Mn) of at most 4, more preferably at most 3.5, more preferably at most 3, more preferably at most 2.5.

In some embodiments wherein the comonomer is butyl methacrylate, the ethylene copolymer according to the invention has $M_w$ of 40-100 kg/mol according to gel permeation chromatography and/or a polydispersity index of at most 3.5, more preferably at most 3, more preferably at most 2.5.

In some embodiments wherein the comonomer is butyl acrylate, the ethylene copolymer according to the invention has $M_w$ of 40-400 kg/mol, according to gel permeation chromatography and/or a polydispersity index of at most 4, more preferably at most 3.5, more preferably at most 3.

The invention further relates to articles comprising the ethylene copolymer according to the invention. The articles may be a film, e.g. upholstery wrap, a disposable glove or a film made by encapsulation; a molded article; an extruded article; an article made by 3D printing; an article made by compounding; a foam; a profile; an adhesive, a bitumen modifier; a sealant or a polymer alloy.

It is noted that the invention relates to all possible combinations of features described herein, preferred in particular are those combinations of features that are present in the claims. It will therefore be appreciated that all combinations of features relating to the composition according to the invention; all combinations of features relating to the process according to the invention and all combinations of features relating to the composition according to the invention and features relating to the process according to the invention are described herein.
It is further noted that the term 'comprising' does not exclude the presence of other elements. However, it is also to be understood that a description on a product/composition comprising certain components also discloses a product/composition consisting of these components. The product/composition consisting of these components may be advantageous in that it offers a simpler, more economical process for the preparation of the product/composition. Similarly, it is also to be understood that a description on a process comprising certain steps also discloses a process consisting of these steps. The process consisting of these steps may be advantageous in that it offers a simpler, more economical process.

The invention is now elucidated by way of the following examples, without however being limited thereto.

Examples

The reagents used in the experiments described below are listed in table 1:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>purity / class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td>Ethylene</td>
</tr>
<tr>
<td></td>
<td>3.0, catalytically purified</td>
</tr>
<tr>
<td>n-butyl acrylate</td>
<td>&gt;99 %*</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>99 %**</td>
</tr>
<tr>
<td>ATRP initiator</td>
<td>Methyl-2- bromopropionate</td>
</tr>
<tr>
<td></td>
<td>(MBBrP)</td>
</tr>
<tr>
<td></td>
<td>98 %</td>
</tr>
<tr>
<td>ATRP catalyst</td>
<td>Copper bromide (II) - CuBr₂</td>
</tr>
<tr>
<td></td>
<td>99 %, purified</td>
</tr>
<tr>
<td></td>
<td>Tris- (2-pyridylmethyl)amine</td>
</tr>
<tr>
<td></td>
<td>(TPMA)</td>
</tr>
<tr>
<td></td>
<td>98%</td>
</tr>
<tr>
<td>Reducing Agents</td>
<td>ascorbic acid</td>
</tr>
<tr>
<td></td>
<td>reagent grade</td>
</tr>
<tr>
<td></td>
<td>α, α’-</td>
</tr>
<tr>
<td></td>
<td>Azobisisobutyronitrile (AIBN)</td>
</tr>
<tr>
<td>Others</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td></td>
<td>99.6 %</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
</tr>
<tr>
<td></td>
<td>99+% , distilled under nitrogen</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
</tr>
</tbody>
</table>
* Contains 10-60 ppm monomethylether hydroquinone which is removed by basic alumina column
** Contains 10 ppm monomethylether hydroquinone which is removed by basic alumina column

The high pressure copolymerizations were performed in a high pressure reactor with inner volume of 100 mL used in batch mode and operated at 2000 bar and 90°C. Stirring was operated by a double blade stirring rotor. Heating of the reactor was implemented by two removable heating sleeves from WEMA providing 1200 W each. Temperature was measured by a type-K thermocouple which is attached to the reactor. The regulating mechanism was performed by a eurotherm regulating unit. Furthermore, a type-K thermocouple was applied inside the reactor to monitor the reaction mixtures temperature. Pressure was measured above the reactor by a Burster pressure transducer.

For all examples listed in table 2, reagents (except ethylene) were fed in the reactor by a separate injection system. It contains a pipe system with a variable injection volume. The solutions to be injected are comonomer and initiator (MBrP), catalyst (CuBr₂+TPMA) in acetonitrile and reducing agent (AIBN or ascorbic acid) in acetonitrile or water. They were prepared in a flask with septum by degassing it with nitrogen for 20 minutes. The solutions were added to the reaction mixture by using certain high pressure injection pipe. After the targeted pressure of 2000 bar was reached the ethylene feed was stopped. The solution of the comonomer and ATRP initiator (MBrP) was injected first, the catalyst solution (CuBr₂+TPMA) was injected second and the solution of the reducing agent/free radical initiator was subsequently injected. For the comparative experiments (1 and 5: free radical copolymerization), only comonomer and AIBN were injected. After a reaction time of 2h, the reaction solution was depressurized and the obtained polymer was collected. The reactor was flushed with 1500 bar ethylene for ten minutes to collect the remaining polymer.

The conversion was calculated according to the amount of comonomers in the feed and the amount of polymer obtained. The obtained polymers were characterized by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR).

A high temperature GPC (PolymerChar) equipped with 4 detectors, namely two
infrared (IR) detectors, one viscosity detector with four capillaries (H502) and dilution chamber and one multi angle light scattering (MALS) detector manufactured by Wyatt with 18 possible angles of incidence (Wyatt DAWN Heleos II) was employed to characterize the molecular weight distribution of the polymers. For injecting the samples, an autosampler Agilent 1200 was used. The GPC has five columns, four are high temperature separating columns. The first column is a Shodex-UT-G protecting column with a particle size of 30 μm. Three of the four high temperature columns are Shodex UT 806M columns with a maximum particle size of 30 μm and a maximum pore size of 10,000 Å. The last high temperature column is a Shodex UT 307 column with a maximum particle size of 30 μm and a maximum pore size of 20,000 Å.

For a GPC measurement 10-20 mg of polymer were dissolved in 1,2,4-trichlorobenzene (TCB). This yields a concentration of 1-2 mg/mL. The autosampler added 8 mL of TCB and heated the solution up to 160 °C in a heated zone for 60-90 mins. It injected 190 μL into the systems and the flow rate of the mobile phase (TCB) constituted 1.0 mL/min which resulted in an analyzing period of 60 mins. The temperatures of the columns and detectors were adjusted to 150 °C. The entire CH-signal from IR-detector (IR5) was used as concentration detector. Analysis was performed using calibrating standards of polystyrene/polyethylene with analysis software PSS WinGPC Unity 7.4.0.

NMR was performed at high temperature in a 100/400 MHz (13C/1H) spectrometer with tempering package with a range from 100 °C to +200 °C. It takes 8000 scans at 100 °C with a pulse relaxation delay of 10s. The spectra are decoupled by inverse gating to make it possible to integrate them. For a NMR measurement 3-4 wt.% polymer were dissolved in 1,1,2,2-Tetrachloroethane-d₂ (C₂D₂Cl₄). To dissolve the polymer the NMR tube was put in a 100 °C heating block for 2 hours and the solution was mixed and heated again. Comonomer content in the final polymer (mol %) was measured by integration of characteristic peaks of a given comonomer.
Table 2. Initial conditions for the polymerization experiments. Pressure 2000 bar. Temperature 90°C

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<tr>
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<th>comonomer</th>
<th>Ethylene (g)</th>
<th>[MBrP] (mol ppm)</th>
<th>[AIBN] (mol ppm)</th>
<th>[CuBr₂] (mol ppm)</th>
<th>[TPMA] (mol ppm)</th>
<th>[ascorbic acid] (mol ppm)</th>
<th>[comon] (mol%)</th>
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<td>1</td>
<td>free radical</td>
<td>butyl methacrylate</td>
<td>50.2</td>
<td>0</td>
<td>53.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.7</td>
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<td>2</td>
<td>ICAR ATRP</td>
<td>butyl methacrylate</td>
<td>49.5</td>
<td>160.5</td>
<td>51.7</td>
<td>57.0</td>
<td>113.4</td>
<td>0</td>
<td>2.8</td>
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<tr>
<td>3</td>
<td>ARGET ATRP</td>
<td>butyl methacrylate</td>
<td>49.8</td>
<td>167.1</td>
<td>0</td>
<td>68.7</td>
<td>157.4</td>
<td>509.3</td>
<td>2.7</td>
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<td>ARGET ATRP</td>
<td>butyl methacrylate</td>
<td>49.4</td>
<td>160.3</td>
<td>0</td>
<td>58.5</td>
<td>136.8</td>
<td>738.6</td>
<td>2.8</td>
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<td>0</td>
<td>0</td>
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<td>49.1</td>
<td>166.3</td>
<td>58.9</td>
<td>73.6</td>
<td>171.1</td>
<td>0</td>
<td>3.3</td>
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<td>49.1</td>
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<td>705.0</td>
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<td>47.2</td>
<td>169.0</td>
<td>0</td>
<td>74.1</td>
<td>172.2</td>
<td>750.2</td>
<td>3.3</td>
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</table>

*: experiment at a temperature of 130°C

5 Table 3. Results

<table>
<thead>
<tr>
<th>#</th>
<th>process</th>
<th>comonomer</th>
<th>Conversion (%)</th>
<th>Comonomer in final polymer (mol-%)</th>
<th>Mw (g/mol)</th>
<th>PDI = Mw/Mn</th>
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<tr>
<td>1</td>
<td>free radical</td>
<td>butyl methacrylate</td>
<td>29.56</td>
<td>21.21</td>
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<td>ICAR ATRP</td>
<td>butyl methacrylate</td>
<td>18.3</td>
<td>27.06</td>
<td>4.20E+04</td>
<td>2.63</td>
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<td>3</td>
<td>ARGET ATRP</td>
<td>butyl methacrylate</td>
<td>12.9</td>
<td>57.64</td>
<td>5.43E+04</td>
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<td>ARGET ATRP</td>
<td>butyl methacrylate</td>
<td>11.3</td>
<td>63.29</td>
<td>7.32E+04</td>
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<td>free radical</td>
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<td>3.19</td>
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<td>15.3</td>
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<td>4.85E+04</td>
<td>2.39</td>
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</table>

In all experiments, ethylene copolymer was successfully prepared. It can be understood that ethylene copolymers obtained by the process according to the
invention (Ex 2-4 and 6-8) has a higher comonomer incorporation than the ethylene copolymers obtained by free radical copolymerization at similar conditions (Ex 1 and 5). The use of similar concentrations of comonomer resulted in ethylene copolymers with a higher amount of incorporated comonomer in the ethylene copolymer, according to the invention. Further, the process according to the invention resulted in a copolymer with a lower PDI than that obtained by free radical polymerization.
Claims

1. A process for preparing an ethylene copolymer by copolymerizing ethylene and at least one comonomer at pressures in the range of from 150 MPa to 350 MPa and temperatures in the range of from 50°C to 350°C by:
   (i) a process in the presence of a system initially consisting of an initiator having a radically transferable atom and a catalyst of a transition metal complex or
   (ii) a process in the presence of a system initially consisting of an initiator having a radically transferable atom, a catalyst of a transition metal complex and a reducing agent,
   wherein the amount of the at least one comonomer in the ethylene copolymer is 0.05-65 mol%.

2. The process according to claim 1, wherein the copolymerization is performed by process (ii).

3. The process according to claim 2, wherein the reducing agent is a free radical initiator.

4. The process according to claim 3, wherein the free radical initiator selected from the group consisting of acyl peroxides, benzoyl peroxides, alkyl peroxydes, cumyl peroxides, tributyl peroxides, hydroperoxides, cumyl hydroperoxide, tert-butyl hydroperoxide, peresters, tert-butyl perbenzoate, alkyl sulfonyle peroxides, dialkyl peroxydicarbonates, diperoxyketals, ketone peroxides, 2,2'-azobisisobutyronitrile ("AIBN"), 2,2'-azobis(2,4-dimethyl peranenitrile), and 1,1'-azobis (cyclohexane-carbonitrile).

5. The process according to claim 2, wherein the reducing agent does not participate as an extra source of radicals in the polymerization process.

6. The process according to claim 5, wherein the reducing agent is an organic compound selected from the group consisting of alkylthiols, mercaptetoethanol, enolizable carbonyl compounds, ascorbic acid, acetyl acetone, camphorsulfonic acid, hydroxy acetone, reducing sugars, monosaccharides, glucose, hydrazine, aldehydes, and derivates of any thereof; or Cu⁰ or tin(II) 2-
ethylhexanoate.

7. The process according to any one of claims 2-6, wherein the amount of the transition metal salt is 10-200 mol/ppm with respect to the total of the ethylene and the at least one comonomer to be copolymerized.

8. The process according to any one of the preceding claims, wherein the at least one comonomer is selected from the group consisting of α,β-unsaturated C₃-C₆-carboxylic acids, in particular maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid and crotonic acid; derivatives of α,β-unsaturated C₃-C₆-carboxylic acids, e.g. unsaturated C₃-C₁₅-carboxylic esters, in particular esters of C₃-C₆-alkanols, in particular methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, or anhydrides, in particular methacrylic anhydride, maleic anhydride or itaconic anhydride; 1-olefins such as propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene or 1-decene; cyclic olefins such as cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, cyclononene, cyclodecene, 1-methyl-1-cyclohexene, 3-methyl cyclohexene, alpha-pinene or norbornene; vinyl monomers such as vinyl carboxylates, particularly preferably vinyl acetate, or styrene; and 1,4-butanediol dimethacrylate, hexanediol dimethacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, dodecanediol dimethacrylate, glycerol dimethacrylate, 1,4-butanediol diacylate, hexanediol diacylate, ethylene glycol diacylate, 1,3-butylene glycol diacylate, dodecanediol diacylate, glycerol diacylate, poly(ethylene glycol) dimethacrylate, poly(propylene glycol) dimethacrylate, poly(ethylene-propylene-glycol) dimethacrylate, 1,4-butanediol divinyl ether, poly(ethylene glycol) divinyl ether, di(ethylene glycol) divinyl ether, 1,4-hexadiene, 1,7-octadiene, 1,9-decadiene and 1,13-tetradecadiene.

9. The process according to any one of the preceding claims, wherein the at least one comonomer is selected from the group consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, methyl
acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate and tert-butyl acrylate.

10. The process according to any one of the preceding claims, wherein the amount of the at least one comonomer with respect to the total of the ethylene and the at least one comonomer to be copolymerized is 0.001-10 mol%.

11. The process according to any one of claims 1-10, wherein the comonomer is butyl methacrylate, and the ethylene copolymer has Mw of 40-100 kg/mol according to gel permeation chromatography and/or a polydispersity index of at most 3.5, more preferably at most 3, more preferably at most 2.5.

12. The process according to any one of claims 1-10, wherein the comonomer is butyl acrylate, and the ethylene copolymer has Mw of 40-400 kg/mol according to gel permeation chromatography and/or a polydispersity index of at most 4, more preferably at most 3.5, more preferably at most 3.

13. The process according to any one of the preceding claims, wherein the ethylene copolymer has a density of 900 to 1100 kg/m³, for example 905 to 1000 kg/m³, 910 to 990 kg/m³, 915 to 970 kg/m³, 918 to 960 kg/m³ or 920 to 950 kg/m³, according to ISO1183.

14. The ethylene copolymer obtained by or obtainable by the process according to any one of the preceding claims.

15. An article comprising the ethylene copolymer according to claim 14, wherein preferably the article is a film, e.g. upholstery wrap, a disposable glove or a film made by encapsulation; a molded article; an extruded article; an article made by 3D printing; an article made by compounding; a foam; a profile; an adhesive, a bitumen modifier; a sealant or a polymer alloy.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
Inv. C08F2/38 C08F210/02 C08F220/18

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

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<td>ISSN: 0002-7863, DOI: 10.1021/ja011331u, tables 1,2, ---, ---</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"Z" document member of the same patent family

Date of the actual completion of the international search
9 January 2017

Date of mailing of the international search report
18/01/2017

Authorized officer
Nikolai, Joachim
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