(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 February 2015 (19.02.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/022248 A1

(51) International Patent Classification:
C08K 5/20 (2006.01) *C08L 67/00* (2006.01)
C08L 23/02 (2006.01)

(21) International Application Number:
PCT/EP2014/066897

(22) International Filing Date:
6 August 2014 (06.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13180409.8 14 August 2013 (14.08.2013) EP

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2015/022248 A1

(54) **Title**: NUCLEATING AGENTS FOR POLYESTERS AND POLYOLEFINS

(57) **Abstract**: Use of at least one compound for crystallization of polyester or polyolefin polymers, characterized in that the compound comprises two hydrogen bonding motifs, a linker connecting said hydrogen bonding motifs and side arms R and R' bound to the opposite of the hydrogen binding motifs, wherein each hydrogen bonding motif resides in a molecular plane and wherein the linker between the hydrogen bonding motifs is chosen such that one of the hydrogen bonding motifs resides in a different molecular plane than the other hydrogen bonding motif(s). They work effectively in promoting the crystallization of a range of polymers, and obtained crystallized polymers have a good transparency and retain a high molar mass.

Nucleating agents for polyesters and polyolefins

Description:

The interest in semi-crystalline polymeric materials has increased rapidly in recent decades. Among the polymeric materials, polyolefins and polyesters are very popular materials. The main factors responsible for the growth in consumption are the inherent versatility of these polymers and the ease with which they can be processed. Such polymers can be used for a large variety of products, as e.g. packaging products, textiles, stationary, containers and automotive components. The properties and the morphology of the semi-crystalline polymers mainly depend on the molecular structure, processing additives and the processing conditions.
When semi-crystalline polymers crystallize from the melt (typically during the cooling phase of a process), lamellae organize from a primary nucleus to form complex macro-structures called spherulites. These spherulites continue to grow until they impinge on an adjacent spherulite at which point the growth ceases. Properties of the polymers, including optical and physical characteristics depend on the end size of the spherulite structures, i.e. the crystal structure of the polymer.

Furthermore, for crystal growth to start a process called nucleation has to occur: this is basically the formation of a focal center around which the lamellae can organize themselves. These nucleation sites can either be imperfections or inconsistencies in a polymer chain or foreign particles in the melt. Nucleation involves the addition of a foreign phase presenting a new surface on which crystal growth can occur. Typically, this foreign phase takes the form of a nucleating agent.
In nucleated polymers, crystallization occurs earlier in the cooling process and happens at a faster rate. This allows decreased cooling time of the polymer. Also,

nucleation density is much higher and crystal spherulite size is much smaller. The crystallization status also influences other semi-crystalline polymer properties, as e.g. transparency.

Nucleating agents for polyesters and polyolefins are known.

US 2005209377A1 discloses the use of nucleants for the crystallization of thermoplastic polyester, especially polybutylene succinates, polycaprolactones, polyhydroxyalkanoates, polyglycolic acids, polylactic acids, and combinations thereof. The nucleant includes compounds with a nitrogen-containing heteroaromatic core, e.g. pyridine, pyrimidine, pyrazine, pyridazine, triazine, or imidazole. Preferably it contains the triazine cyanuric acid.

CN101857715(A) achieves the quick crystallization of PLA with an organic compound comprising four amide motifs and modified benzyl side arms. The use of dicarboxylic acid chlorides as starting compounds makes the synthesis of this model compound prone to side reactions resulting in multiple time consuming purification steps. Furthermore, these nucleating agents use benzoic hydrazide as starting compound which is known to be highly toxic and is suspected to be carcinogenic.

EP1477526A1 describes the use of amide compounds in the crystallization of PLA resins. Potentially, also a compound with multiple amide motifs can be used. However, the nucleating agent has an aromatic side arm. Such side arms can cause yellowing of the final polymer product and compounds comprising them are often toxic. Furthermore, the amide motifs reside in one molecular plane because no linker is placed between the amide motifs or (e.g. in the case of ethylene bisstearamide) an unmodified ethyl linker. Ethylene bisstearamide has also been described in WO2009/064851A2.

EP2319882A1 pertains to nucleating agents comprising e.g. four carbamate (i.e. urethane) groups, or one hydrogen bonding motif (e.g. hydrazides) with e.g. cycloaliphatic side arms.

US201113101330 discloses a polypropylene resin composition comprising a polypropylene polyethylene copolymer and an amide compound as nucleating agent. In the nucleating agent the amide groups are substituents of an aromatic ring or in the form of a propane tricarboxylic acid triamide.

EP0557721 and EP1431335 describe bisamide compounds for the crystallization of polypropylene. However, the side arms comprise aromatic or cyclic groups. Aromatic arms have the disadvantage that they can cause yellowing of the final polymer product and compounds comprising them are often toxic.

The combination of nucleation efficiency, decrease in crystallization half-time, and desired transparency of the product in the presence of the nucleating agents in the prior art is not optimal.

The aim of present invention is to overcome at least in part the disadvantages that lie in the use of known nucleating agents and to provide alternative nucleating agents for polyesters and polyolefins.

To achieve this, the present invention describes using a class of compounds as nucleating agents for polyesters and polyolefins, which compounds have a high nucleation efficiency and a melting temperature which can be adjusted to the melting temperature of the specific polymer. Also, due to the use of the nucleating agents the half-time of crystallization of the polymer is decreased. The nucleating agents of present invention allow for a high onset crystallization temperature and a high degree of crystallinity. Additionally, the inventive use of the nucleating agents results in good transparency, good structural order of the crystallized polymers and polymers which retain their molar mass.
Another objective of this invention is to provide a process for crystallization of polyester or polyolefins wherein the nucleating agent has a high nucleation efficiency.

Furthermore, a composition of the polymer and nucleating agents with high nucleation efficiency is provided and films, moldings, composite materials, extrusion- or injection-molded products or elongated products comprising the composition.

Throughout this description the terms ‘nucleating agent’ and ‘compound’ are used interchangeably.

These tasks are solved by using at least one compound for crystallization of polyester or polyolefin polymers, characterized in that the compound comprises a core and side arms R and R’ flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif;
wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:
(i) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;
(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;
(iii) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:
    (i) an alkyl group comprising 1 to 8 carbon atoms,
    (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,
    (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,
    (iv) a halogen or oxygen,
    (v) a monovalent functional group; or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;

and wherein the side arms R and R' are independently of each other chosen from:

(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;

(iii) one of the following esters:

- X-Ester-Y,
- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein

X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

In one embodiment the nucleating agent according to the invention consists of said core and said flanking side arms R and R'.

The hydrogen bonding motifs present in the nucleating agent are the driving force for crystallization of the nucleating agent. Two hydrogen bonding motifs are present in the nucleating agent. The hydrogen bonding motif preferably is an amino carboxy motif.

The hydrogen bonding motifs preferably are chosen from an amide motif (-C(O)-NH- or inverted), an oxalamide motif (-NH-C(O)-C(O)-NH-), a hydrazide motif (-C(O)-NH-NH-C(O)-), an urethane motif (-O-C(O)-NH-, or inverted) or an urea motif (-NH-C(O)-NH-).

In the embodiment where the hydrogen bonding motif is an oxalamide or hydrazide in fact four hydrogen bonding moieties are present. This is advantageous.

The hydrogen bonding of the compounds described for the use for the crystallization of polyolefins or polyesters is very strong and leads to self-assembly of compound molecules which form fibrillar networks that act as crystallization nucleus for the polymer. Surprisingly, it was found that it is advantageous if the hydrogen bonding motifs present in the compound reside in different molecular planes. The choice of the linker between the hydrogen bonding motifs and the combination of hydrogen bonding motifs in the core influences the molecular, planar position of the hydrogen bonding motifs within the compound. The hydrogen bonding motifs themselves form a molecular plane, e.g. in an amide motif all atoms (-C(O)-NH-) are positioned in one molecular plane. Preferably, different plane means non-parallel planes, such that at least one hydrogen bonding motif resides in a plane positioned at an angle compared to the plane of another hydrogen bonding motif. In this way, the hydrogen bonding motifs are not planar, but anti planar or periplanar positioned to each other. The angle α between the plane of one hydrogen bonding motif and the plane of another one is preferably chosen to be: $0° < \alpha < 180°$, more preferably $5° < \alpha < 175°$ (or the corresponding $360° - \alpha$ angle). The angle is determined by placing a fictional line in the plane of each hydrogen bonding motif. The line runs along the main extension direction of the plane and can be defined as the line from the atom of the hydrogen bonding motif which is connected to the side arm R or R' to the atom which is connected to the linker moiety. Where the fictional, extended lines of two planes (i.e. from two different hydrogen bonding motifs) meet the angle is determined.
It is believed that the deviating planes of the hydrogen bonding motifs within one nucleating agent molecule disturb the formation of large three dimensional crystal aggregates. Advantageously, in consequence smaller crystal aggregates are formed which can form fibrillar networks and improve the transparency of the crystallized polymer.

Therefore, the nucleating agents of present invention differ from prior art nucleating agents where hydrogen bonding motifs reside in the same molecular plane. Such prior art nucleating agent is e.g. ethylene bisstearamide, where two amide motifs are connected by an ethyl linker.

The angle between the planes of the hydrogen bonding motifs can be influenced by choosing the linker between the hydrogen bonding motifs carefully. Preferably, the linker is chosen from: (i) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;

(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;

(iii) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:

  (i) an alkyl group comprising 1 to 8 carbon atoms,
  (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,
  (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,
  (iv) a halogen or oxygen,
  (v) a monovalent functional group or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker.

That means that in the case where the core comprises different hydrogen bonding motifs either one of linkers (i) – (iv) is chosen, but when the core comprises the same hydrogen bonding motifs either one of linkers (i) –(iii) is chosen.

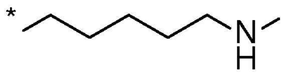
The linker doesn’t comprise any of the hydrogen bonding motifs. That means that the linker does not contain an amide, oxalamide, hydrazide, urethane or urea

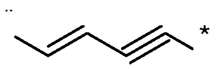
motif. The linker is the part of the molecule between any of these motifs, i.e. excluding the atoms that are part of the hydrogen bonding motifs.
When defining the linker as part of the molecule of the nucleating agent the longest possible hydrogen bonding motifs should be defined (e.g. a hydrazide instead of two amide motifs) and the chain between those motifs is defined as the linker.

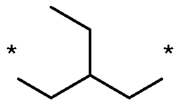
Preferably, the linker comprises between 1 and 8 backbone atoms, more preferably between 1 and 6 backbone atoms and even more preferably between 1 and 4 backbone atoms.
An unsaturated aliphatic hydrocarbon group is part of an alkene chain and comprises 1 to 12 carbon atoms and a corresponding number of hydrogen atoms, provided that at least one carbon-carbon bond is unsaturated (e.g. -CH=CH-, or –C≡CH-). When an unsaturated aliphatic hydrocarbon group is chosen the number of unsaturated carbon bonds preferably is uneven, for example 1 or 3.
In another embodiment an alkanediyl group is chosen where at least one of the carbons is replaced by a moiety comprising N, P, S or O. An alkanediyl is a series of divalent radicals of the general formula C_nH_{2n} derived from aliphatic hydrocarbons. It can be branched. The heteroatom moieties are e.g. –S-, -O-, -O-P(O)-O-, -NH-, O=S=O, N-CH_3, ester (-C(O)O- or -O-C(O)-) and thioester (e.g. -C(O)-S-). In another embodiment also an alkanediyl chain is chosen as linker, however, at least one of the hydrogen atoms on the alkanediyl group is substituted. Possible substituents are alkyl groups, halogens, oxygen (resulting in a keto group:-C(O)-), monovalent organic functional groups or alkyl groups where at least one of the carbon atoms is substituted by a divalent organic functional group, a heteroatom, a halogen or a monovalent organic functional group. Monovalent organic functional groups are e.g. amino (-NH_2), thio (-SH) and hydroxyl (-OH) groups. Divalent organic functional groups are e.g. ester (-C(O)-O- or O-C(O)-), ketone (-C(O)-) or amide groups (-C(O)-NH-).
Preferably, in a linker comprising substituted hydrocarbons an uneven number of substituents for carbon atoms or hydrogen atoms is present.

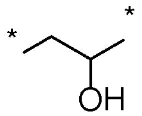
The linker length influences the peak melting and crystallization temperature of the compound in such a manner that a longer linker decreases the melting temperature while a shorter linker increases the melting temperature. Therefore, the length and structure of the linker can also be used as a tool to design the optimal compound for a specific polymers matrix in terms of solubility and melting temperature. Control of the melting point is useful to use the compound (or combination of compounds) as efficient nucleating agent for different polymers which have different melting temperatures. High melting temperatures of nucleating agents are advantageous because they improve the nucleation efficiency of the nucleating agent.

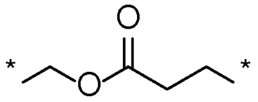
Possible linkers are e.g.:

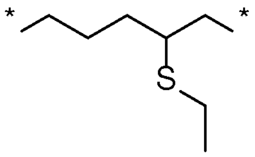












(* denotes where the linker is bound to the hydrogen bonding motifs)

The arms R and R’ can be chosen in a way to improve the miscibility with the polymer. A good miscibility of the nucleating agent with the polymer causes a homogenous distribution of the nucleating agent in the polymer matrix and leads to better crystallization. This is obtained by designing the arms to be similar to the molecular configuration of the polymer. When R, R’ and the molecular configuration of the polymer to be crystallized are similar, the crystal structure of the compound suppresses the nucleation barrier and increases the nucleation efficiency of the polymer, thus increasing the crystallization rate. The side arms R and R’ also influence the melting temperature of the compounds described in the invention.

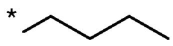
In a preferred embodiment the side arms R and R’ are the same such that a compound with symmetric ends or side arms is obtained.

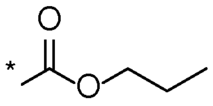
In one embodiment at least one of the side arms R and R’ is chosen from an alkyl group with a total carbon number between 2 and 20, preferably with a total carbon number between 2 and 10 and more preferably with a total carbon number between 2 and 8, even more preferably with a total carbon number between 2 and 6 or 2 and 4.

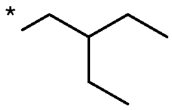
In another embodiment the hydrogen atoms on the saturated aliphatic hydrocarbon group and/or on the alkyl side arms R or R’ are substituted by methyl, ethyl or alkyl groups of up to 8 carbon atoms, where the total number of all carbon atoms of the saturated aliphatic hydrocarbon group or the alkyl group is not higher than 20. This means that in this embodiment at least one of the arms R or R’ comprises a branched alkyl group and/or a branched saturated aliphatic hydrocarbon group.

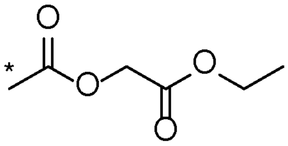
In a preferred embodiment the arms R and R’ do not comprise cyclic or aromatic structures. In a preferred embodiment the nucleating agent does not comprise cyclic aliphatic or aromatic groups.

Possible side arms R and R’ are:









(* denotes where the presented linker is bound to the core, i.e. a hydrogen bonding motif)

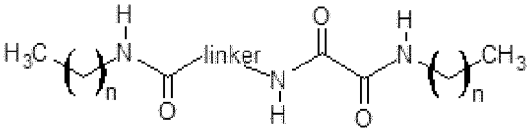
An ester is a group containing a carbonyl connected to an oxygen atom (-C(O)-O-) or an oxygen atom connected to a carbonyl group (-O-C(O)-).

Side arms comprising one or multiple ester groups are a preferred embodiment.

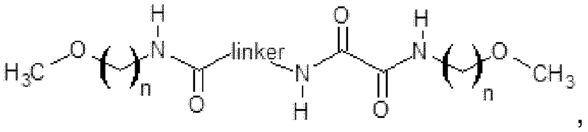
The saturated aliphatic hydrocarbon group (referred to as X) of the side arms R and R' comprising 1 to 20 carbon atoms is part of an alkane chain and only consists of carbon and hydrogen atoms. All carbons are bound to each other by single carbon bonds. X includes unbranched carbon chains and branched carbon chains, i.e. isomers where the total number of carbon atoms is limited to 20.
The saturated aliphatic hydrocarbon group is bound to the other moieties of the nucleating agent by two bonds.
Examples of the aliphatic hydrocarbon group are: $-CH_2-CH_2-CH_2-$ or $-CH_2(CH_3)-CH_2-$.
For example, the saturated aliphatic hydrocarbon group is bound to a methyl group or H (i.e. Y) on one side and to an ester group or the bisoxalamide motif, i.e. the core of the nucleating agent on the other side.

An alkyl is a monovalent aliphatic moiety with a total number of carbon atoms between 1 and 20, i.e. a functional group comprising only carbon and hydrogen atoms derived from an alkane by removing one hydrogen atom. This definition includes unbranched carbon chains and branched carbon chains, i.e. isomers. Examples are: methyl, ethyl, propyl or isopropyl.

For example, a compound according to the invention has one of the following structural formula:



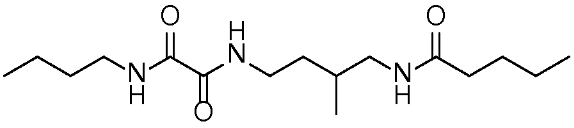
Or:



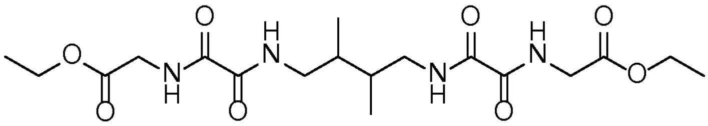
,

where n is between 2 to 5 and any of the described linkers is chosen.

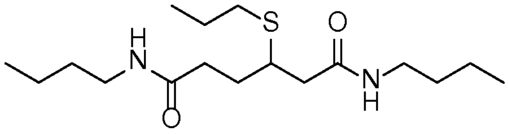
Other nucleating agents according to the invention are:



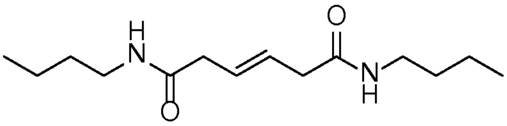
*N*¹-butyl-*N*²-(3-methyl-4-pentanamidobutyl)oxalamide



diethyl 8,9-dimethyl-4,5,12,13-tetraoxo-3,6,11,14-tetraazahexadecanedioate



*N*¹'*N*⁶-dibutyl-3-(propylthio)hexanediamide



(*E*)-*N*¹'*N*⁶-dibutylhex-3-enediamide

The nucleating agents described in present invention are used for the crystallization of polyesters and polyolefins. Preferably, they are used for the crystallization of thermoplastic and thermoelastomeric polymers, as e.g. polypropylene and polypropylene copolymers and polyethylene copolymers from the group of polyolefins.

The nucleating agents of the present invention are less suited and thus not preferred for the crystallization of polyimides. From the group of polyesters the nucleating agents described in present invention are e.g. suitable for the crystallization of polyesters in general, preferably for bio-based polyesters, as e.g. PHA, PLA and furan-based polyesters, produced either conventionally or from natural resources.
For the purpose of this invention polypropylene includes isotactic, syndiotactic and atactic polypropylene, where the tacticity can vary from approximately 60 to 100% in the case of isotactic and syndiotactic polypropylenes.

Polypropylene copolymers for the purpose of this invention include polypropylene-alpha-olefin copolymers and poly(propylene-styrene) copolymers. Examples for suitable alpha-olefins include but are not limited to polyethylene (PE), polybutylene, and poly(4-methyl-1-pentene). The polypropylene copolymers include polypropylene block copolymers and polypropylene random copolymers. The polypropylene copolymers comprise at least 60% propylene units. A preferred polypropylene copolymer is a propylene-ethylene copolymer, where e.g. the amount of ethylene monomers varies between 1 and 10 mole% based on the total amounts of monomers which are used to produce the polymer, preferably between 2 and 5 mole%.
Polyethylene copolymers comprise at least 60% of ethylene units. As co-monomers hexyl, butyl or octyl monomers at an amount of 2-8mole% based on the total amount of monomers can be chosen.
Among the polyesters, the nucleating agents are preferably used for bio-based polyesters as polyhydroxy-alkanoates (PHAs) and poly(lactic) acid (PLA), and furan-based polyesters.
For the purpose of this invention PHA is defined as a polymer comprising various possible PHA monomers known to the person skilled in the art, with varying possible pendant groups in the side chains, including homopolymers, copolymers, terpolymers and higher combinations of monomers, for example including the

following polyhydroxybutyrates: poly-hydroxybutyrate-hydroxyvalerate (PHBHV) and poly-hydroxybutyrate-hydroxyhexanoate (PHBHH).
PLA includes the stereo complexes P(L)LA, P(D)LA and all possible combinations thereof. Depending on the stereo-chemical purity of the monomer feed, the ratio L-LA versus D-LA, PLAs can be obtained with a variety of stereo-chemical purity, from pure P(L)LA and pure P(D)LA to P(D/L)LA copolymers and P(L)LA/P(D)LA stereocomplexes.
Furan-based polymers are obtained by using furan or furan-based aromatic units (e.g. Furan-2,5-dicarboxylic Acid) as building blocks for a esterification.

In one embodiment the polymer to be crystallized is a combination of PHA and PLA. In this combination of polymers, PHA and PLA each can be present in varying percentages based on the total amount of polymer.

The compounds used according to the invention have a peak melting temperature ranging between 100 and 300°C, preferably between 120 and 290°C, more preferably 150 and 280°C.

For the crystallization the compound or the combination of compounds are applied at a concentration of 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% based on the weight of the polymer.
If a combination of compounds is used to crystallize a polyolefin or polyester, said amounts refer to the combined amount of the different compounds. This means that the total amount of nucleating agent added to the polymer can either consist of one nucleating agent or a combination of different nucleating agents according to this invention. If a combination of nucleating agents is used, the total amount of nucleating agents is the same as if one nucleating agent is used. The amount is always based on the weight of the polymer. For example, 0.05wt% of nucleating agent A and 0.05wt% of nucleating agent B result in an amount of 0.1wt% nucleating agent based on the weight of the polymer.

The relative amount of each compound of such a combination of compounds can vary depending on the polymer, copolymer or polymer mixture which is to be crystallized.

In another embodiment the invention relates to a process for crystallization of polyester or polyolefin polymers, comprising the steps of:

(a) mixing the polymer with a compound or a combination of compounds at a first temperature, ranging from 10℃ to 140℃ above the peak melting temperature of the polymer; and

(b) cooling the polymer at a second temperature, ranging from the first temperature to 20℃, characterized in that the compound comprises a core and side arms R and R' flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif; wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:

(i) an alkanediyl chain comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;

(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;

(iii) an alkanediyl chain comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:

    (i) an alkyl group comprising 1 to 8 carbon atoms,
    (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,
    (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,
    (iv) a halogen or oxygen,
    (v) a monovalent functional group; or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;

and wherein the side arms R and R' are independently of each other chosen from:

(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;

(iii) one of the following esters:

- X-Ester-Y,
- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein

X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

In one embodiment the compound has a peak melting temperature ranging between 100 and 300℃, preferably between 120 and 290℃, more preferably 150 and 280℃.

In one embodiment of the process the compound or a combination of compounds is applied at a concentration of 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% based on the weight of the polymer.

Preferably, the first temperature at which the polymer and the nucleating agent(s) are mixed ranges between 10℃ and 140℃, preferably between 20℃ and 120℃, more preferably between 40℃ and 120℃ above the peak melting temperature of the polymer.

The second temperature, i.e. the cooling temperature preferably ranges from 140°C above the peak melting temperature of the polymer to 20°C, preferably from 120°C above the peak melting temperature of the polymer to 20°C. As pointed out before a high crystallization temperature is beneficial for the polymer product and its production.

The cooling occurs at a rate ranging between 1°C /min and 500°C /min, preferably between 10°C /min and 300°C /min, more preferably between 20°C /min and 100°C /min. With an increased cooling rate the nucleation efficiency becomes more evident and it reduces production time.

The use of the nucleating agents according to this invention leads to the assembly of the nucleating agents in a fibrillar structure of small dimension. The presence of the fine fibrillar or network morphology of the nucleating agent enhances the nucleation efficiency of the polymer in comparison with a polymer without nucleating agents or in comparison to a polymer which is nucleated with a nucleating agent that assembles in large three-dimensional aggregates. The dimensions of the fibrillar crystals vary with the crystallization conditions and the chosen combinations of the nucleating agents. Usually, they cannot be observed by optical microscopy (at an enlargement of ca. 1x10 to 1x40). The small, fibrillar dimensions probably increase the surface area and cause also an increase in the number of the nucleation sites. This is likely to lead to an increase in the surface-volume ratio compared to nucleating agents which cause larger, needle-like aggregates. Without being bound by theory this probably improves the crystallization and nucleation efficiency.

The crystal size of the nucleating agent in the polymer matrix can be determined by electron microscopy or atomic force microscopy.

The nucleating agents according to the invention show high nucleation efficiencies. The nucleation efficiency (NE) is defined as the increase of the crystallization temperature of the polymer with the nucleating agent compared to the crystallization temperature without nucleating agent. This is calculated by using equation 1:

$$NE = (T_c - T_{c1}) / (T_{c2\max} - T_{c1}) \times 100$$

where T_{c1} and T_{c2max} are the peak crystallization temperatures of the non-nucleated and self-nucleated polymer, respectively. T_c is the peak crystallization temperature of the polymer with the nucleating agents.

Many polymers crystallize inefficiently without a nucleating agent in industrial processing. The material which can be obtained without nucleating agent is of lower crystallinity and has a lower dimensional stability.
However, with the here described nucleating agents or combinations thereof the onset temperature for crystallization of the polymer is increased. The here described nucleating agents or combinations thereof increase the onset crystallization temperature by at least 5°C, preferably by at least 10°C, more preferably by at least 15°C, or by at least 20°C compared to the polymer or copolymer without any nucleating agent. The specific temperature depends on the specific compound or combination of compounds according to this invention, the amount of nucleating agent and the polymer or copolymer. A higher onset temperature is better for the produced plastics because the mechanical properties of the material are better, the production time is shorter because less cooling has to take place and no or less shrinkage of the crystallized polymer occurs. The high nucleation efficiency provides the desired dimensional stability. Thus, the high onset crystallization temperature of the polymer or copolymer in the presence of the nucleating agents of present invention enables easier processability and a higher dimensional stability of the polymer product.

Present invention is also directed to a composition comprising polyester or polyolefin polymer and at least one compound, characterized in that the compound comprises a core and side arms R and R’ flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif;

wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:

(i) an alkanediyl chain comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;

(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;

(iii) an alkanediyl chain comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:

- (i) an alkyl group comprising 1 to 8 carbon atoms,
- (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,
- (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,
- (iv) a halogen or oxygen,
- (v) a monovalent functional group; or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;

and wherein the side arms R and R' are independently of each other chosen from:

(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;

(iii) one of the following esters:

- X-Ester-Y,
- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,

- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein

X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

The composition comprises 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% of the compound or a combination of compounds based on the weight of the polymer.

In one embodiment films, moldings, composite materials, injection- or extrusion-molded products or elongated products comprise a composition according to this invention. Elongated products include fibers, as e.g. staple fiber, short fiber and continuous fiber, and tapes.

Compositions, i.e. polymers crystallized with nucleating agents or a combination of compounds according to the invention have a good transparency. Also, the obtained crystallized polymers retain a high molar mass. Both properties are advantageous for the production of articles made from polymeric materials.

The following examples describe the invention in more detail but by no means limit the scope of the invention.

Synthesis of compound & methods for measuring the characteristics of compound and compound-polymer composition

1. Synthesis of N-hexyl-N'-[2-(hexylamino)-2-oxo-ethyl]oxamide (NA1)

Hexylamine (99 %), diethyloxalate (99 %), glycine (99 %), THF, EtOH and hexane were purchased from Acros and used as received. 1,1'-carbonyldiimidazole (> 97 %) was bought from Sigma-Aldrich, as well as diethylether and NaOH pellets (> 98 %). Silica gel with a pore size of 60 Å and 70-230 mesh was obtained from Fluka. DMF (Acros) was purified by distillation and stored on 4 Å molecular sieves.

All reactions were carried out under nitrogen.

a. Synthesis of intermediate (1)

A solution of 17.45 g (0.1724 mol) hexylamine in 100 ml THF was added slowly to 251.95 g (1.724 mol) of diethyloxalate stirred at 0 °C using a dropping funnel. A white precipitate was formed during the reaction. When all the hexylamine was added, the mixture was allowed to react for 24 hours at room temperature. The majority of the diethyloxalate excess was removed by rotary evaporation. Column chromatography with 70/30 hexane/diethylether as eluent was applied to remove the last traces of diethyloxalate from the reaction mixture. Once the diethyloxalate was removed, the eluent was changed to 100 % diethylether to elute product (1). After removal of the solvent from the collected fractions, product (1) was obtained as a light yellow oil.

The molecular structure of the intermediate was analyzed by ^{1}H-NMR and showed the following parameters: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.90 (t, 3H, $C\mathit{H_3}CH_2O$-), 1.32 (br, 6H, $-NH-CH_2-CH_2-(C\mathit{H_2})_3-CH_3$), 1.40 (t, 3H, $-NH-(CH_2)_5-C\mathit{H_3}$), 1.58 (br, 2H, $-NH-CH_2-C\mathit{H_2}-(CH_2)_3-CH_3$), 3.34 (q, 2H, $-NH-C\mathit{H_2}-$), 4.37 (q, 2H, $CH_3C\mathit{H_2}O$-), 7.12 (s, 1H, $-N\mathit{H}-$)

TLC (normal phase, eluent 70/30 hexane/diethylether, color agent $KMnO_4$) : R_f = 0.25

b. Synthesis of intermediate (2)

Intermediate (2) was prepared according to a procedure modified from Appl. Organometal. Chem. 2007; 21: 1013-1021.

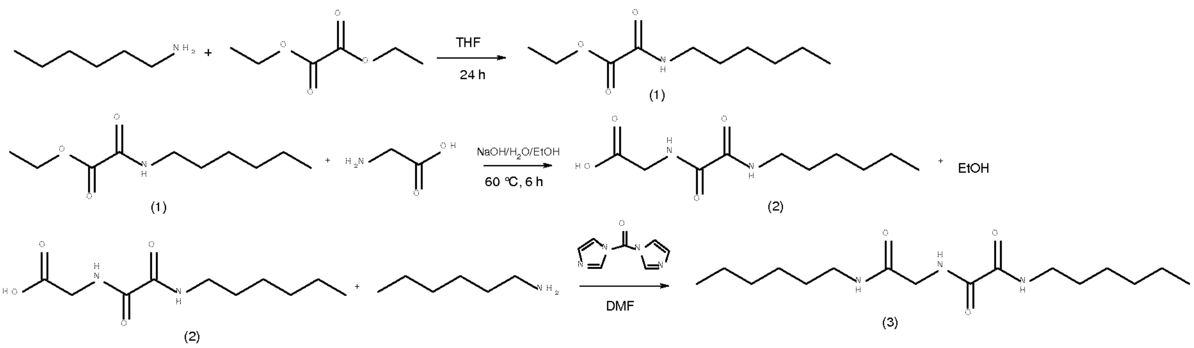
3.90 g (0.052 mol) of glycine was dissolved in 65 ml water and 2.0798 g (0.052 mol) of NaOH pellets were used for neutralization of the carboxylic acid. 10.47 g (0.052 mol) of intermediate (1) dissolved in 39 ml EtOH was added to the aqueous solution. The reaction mixture was heated to 60 °C for 5 h. Afterwards, the mixture was cooled to 0 °C and 4.31 ml 37 % HCl (0.052 mol) was added to desalt the carboxylic acid group. The resulting white crystals were filtered and rinsed with ice cold water. The white crystals were dried by lyophilization.

The crystal structure of the intermediate was analyzed by ^{1}H-NMR and showed the following ^{1}H proton chemical shifts: ^{1}H-NMR (DMSO-d_6, 300 MHz) δ (ppm): 0.86 (t, 3H, CH_3CH_2-), 1.26 (br, 6H, CH_3-$(CH_2)_3$-), 1.46 (q, 2H, CH_3-$(CH_2)_3$-CH_2-), 3.14 (t, 2H, -CH_2CH_2NH-), 3.82 (d, 2H, -NH-CH_2-(C=O)-), 8.76 (s, 1H, -NH-), 8.84 (s, 1H, -NH-)

c. Synthesis of end product N-hexyl-N'-[2-(hexylamino)-2-oxo-ethyl]oxamide (NA1)

0.1842 g (0.0008 mol) of intermediate (2) was dissolved in 6.4 ml dry DMF and 0.1427 g (0.00088 mol) of 1,1'-carbonyldiimidazole was added to this solution. The mixture was allowed to stir at room temperature for 15 minutes, after which 0.11 ml (0.0008 mol) hexylamine was added dropwise. The reaction continued for 12 h at room temperature, after which the mixture was precipitated in an excess of 1 M HCl. The white powder was filtered off and rinsed successively with 1 M HCl and with water. The final product (white crystals) was dried by lyophilization and melts at 199°C.

The molecular structure of NA1 was analyzed by ^{1}H-NMR and showed the following following ^{1}H proton chemical shifts: ($CDCl_3$, 300 MHz) δ (ppm): 0.82 (t, 6H, 2 x CH_3-), 1.22 (br, 12H, 2 x CH_3-$(CH_2)_3$-), 1.5 (br, 4H, 2 x -CH_2-CH_2-NH-), 3.24 (m, 4H, 2 x -NH-CH_2-), 3.90 (d, 2H, -NH-CH_2-(C=O)-), 5.76 (s, 1H, -NH-), 7.31 (s, 1H, -NH-), 7.94 (s, 1H, -NH-)



2. Melt mixing

Melt mixing of the nucleating agent and the respective polymers was performed using a co-rotating twin screw mini-extruder (DSM Xplore) with sample residence time of 5 min after complete feeding. In the examples different polymers were used as polymers for crystallization tests. The samples were prepared using different amounts of nucleating agents, as indicated in the tables and based on the weight of the polymer. As reference, the crystallization behavior of the polymers without any nucleating agent is shown. The samples were processed at 185 °C or 230 °C.

As polymers were used polypropylene copolymer (PP, RB206MO, from Borealis), poly lactic (L) acid (PLLA, 1010, from Syntera) and polyhydroxy butarate valerate copolymer (PHBV, Mirel, MZ100, Metabolix Inc., comprising ca. 12 mole% of valerate monomers). The polymers were processed at elevated temperatures, as indicated in the tables.

3. Differential Scanning Calorimetry (DSC)

Melting and crystallization of the nucleating agents, and polymers without and with nucleating agent was investigated using DSC (TA Q2000 instrument). The heating and cooling rate was always 10 °C/min with 1 minute of isothermal condition at limiting temperatures. The sample was heated above the melting point and cooled down to -40 °C.

In order to quantify the nucleation efficiency the heat flow upon cooling at 40 °C/min was followed by DSC using a TA Q2000. In order to erase the thermal history the samples were heated at 10°C/min into the melt at 200°C, where the temperature was held for 5 minutes prior to cooling. The enthalpy of crystallization is directly correlated to the crystallinity of the sample, where a high enthalpy accounts for a high crystallinity.

The onset melting temperature is defined as the start of the endothermic process, whereas the peak melting temperature or peak melting point is defined as the peak of the endothermic process recorded by DSC. The onset crystallization temperature is defined as the start of the exothermic process, whereas the peak crystallization temperature is defined as the peak of the exothermic process recorded by DSC.

4. Optical Microscopy

Crystallization measurements were conducted on a Zeiss Axioplan 2 Imaging optical microscope under crossed polarizers with a CD achorplan objective (Zoom) using a magnification of 20 times. A Linkam hotstage (TMS 94) was used to heat the sample into the melt state at 230°C for 5 minutes, after which the sample was cooled to 120°C with 40°C/min. As soon as the temperature of 120°C was reached, micrographs were taken every 10 seconds.

5. Rheology

The viscosity change was measured using isothermal crystallization experiments at the temperature of 120°C, which were carried out using a stress-controlled shear rheometer (TA Instruments, DHR-1) with 25 mm plate-plate setup at an angular frequency of 1 rad/second. In order to erase the thermal history the samples were heated with 5°C/min into the melt state at 200°C, where the temperature was held for 5 minutes prior to cooling to 120°C.

6. Transparency

Transparency measurements were performed on a Shimadzu UV-3102PC UV-VIS-NIR scanning spectrometer. Samples were scanned in the range between 800 to 300 nm^{-1}. The transparency values are shown for the wavelength of 500 nm^{-1}.

Samples were prepared via compression molding (1.5 mm x 50 mm x 12.5 mm) at 210 ℃ (PP-copolymer). Actual thickness of the samples after compression molding was 1.57 mm. The value reflects the light which passes through the sample and therefore a higher value corresponds with better transparency.

Abbreviations and symbols:

NE : Nucleation efficiency (according to equation 1)

T_c /T_c^N : Peak crystallization temperature of the polymer in the presence of the nucleating agent (T_c^N) or of the pristine polymer (T_c)

T_{onset} : Onset of crystallization temperature of the polymer in the presence of the nucleating agent or of the pristine polymer

$t_{0.5}$: Half time of isothermal crystallization of the polymer

ΔH_m : Enthalpy of melting of the polymer

ΔH_c : Enthalpy of crystallization of the polymer

T_{c1} : peak crystallization temperature of the non-nucleated polymer

T_{c2max} : peak crystallization temperature of the self-nucleated polymer

Ref. : reference sample, no nucleating agent added

Visco : time of polymer melt viscosity increase until onset of crystallization, under isothermal conditions

PP: polypropylene ethylene copolymer

PLLA: poly lactic (L) acid

PHBV: polyhydroxy butarate valerate copolymer

PDI: polydispersity index

Mn: number average molar mass (g/mole)

Nucleating agents:

NA1 = N-hexyl-N'-[2-(hexylamino)-2-oxo-ethyl]oxamide

NA2 = N,N′-Ethylenebis(stearamide)

NA3 = Behenamide

NA4 = [3-(octylcarbamoyloxy)-2,2-bis(octylcarbamoyloxymethyl)propyl] N-octylcarbamate

NA5 = N'-benzoylbenzohydrazide

Table 1. Melting temperatures of the used nucleating agents.

Sample	T_m(℃)
NA1	199.00
NA2	144.00
NA3	110.00
NA4	265.98
NA5	237.47

Example 1

The performance of NA1 as nucleating agent according to this invention was tested for three different polymers. More specifically, the crystallization behavior of the respective polymer with NA1 and without any nucleating agent was determined using differential scanning calorimetry (DSC) and viscosity measurements (for rheology analysis). For one example, also optical microscopy was carried out. The polymers as indicated in table 2 were melt-mixed with NA1 or without any nucleating agent and subsequently cooled (as described above). The nucleation efficiency was determined for NA1 in PP as 48%, calculated according to equation 1, with T_{c2max} experimentally determined to be 113℃. The measurement results of the DSC and the rheology analysis are shown in table 2.

Table 2: Crystallization of three different polymers with NA1

Sample	T_C/T_c^N (°C)	T_{onset} (°C)	ΔH_c (J/g)	T_m (°C)	Processing temperature (°C)	Cooling Rate (°C/min)
PHBV	50.13	62.72	66.23	168.48	185	10
PHBV + 0.5 wt% NA1	70.13	92.73	80.06	168.75	185	10
PP	91.9	97.8	7.74	142.22	230	10
PP + 0.3wt% NA1	101.8	108.9	8.11	142.30	230	10
PLLA	95.21	109.28	50.09	173.01	185	10
PLLA + 0.5wt% NA1	98.31	110.85	54.58	173.02	185	10

The enthalpy of crystallization is directly correlated to the crystallinity of the polymer, where a high enthalpy accounts for a high crystallinity. Accordingly, the use of the nucleating agent according to the invention increases the crystallinity for all polymers. The results also demonstrate the increased onset of crystallization upon cooling and the increased crystal growth rate upon cooling from the melt in the presence of the nucleating agent.

For the polypropylene ethylene copolymer sample (PP) also optical microscopy was performed. From optical microscopy it is apparent that the spherulitic growth of the polymer is templated by a fibrillar network, validated at the early start of the polymeric crystal growth (100s). This is demonstrated in Fig. 1 which shows optical micrographs of the polymer crystal growth and final dimensions of the spherulites for the polymer comprising the nucleating agent or without any nucleating agents. In regular intervals (each 10 seconds between 0 and 400 seconds, depicted in Fig. 1 is a selection of those) a picture was taken. In the top panel (NA a, i.e. NA1), the spherulitic dimensions are significantly smaller, which promotes polymer properties such as transparency. Presumably, the spherulites grow on top of the fibrillar network provided by the nucleating agent. In the lower panel (Ref., without nucleating agent) the polymer growth is much slower and much larger spherulites occur.

Example 2 – Comparison of a nucleating agent according to the invention and known nucleating agents for the crystallization of PHBV

The crystallization behavior of PHBV was analyzed after addition of either NA1, NA2, NA3 or NA5. Additionally, the molar mass of the obtained polymer was determined.

NA2 is a nucleating agent consisting of two amide motifs linked by an ethyl group and having alkyl side arms. The linker is not modified. NA2 has been described in EP1477526.

NA3 (behenamide) is a nucleating agent comprising one amide motif.

NA5 is a nucleating agent comprising one hydrazide motif and benzyl rings as side arms. Such nucleating agents comprising ring structures are e.g. known from EP2319882.

The results of the crystallization are shown in table 3.

Table 3. Crystallization of poly(hydroxybutyrate-co-hydroxyvalerate) copolymer (PHBV) with different nucleating agents.

Sample	T_C /T_c^N (°C)	T_{onset} (°C)	Mn (kg/mol)	PDI	Processing temperature (°C)	Cooling Rate (°C/min)
PHBV	50.13	62.72	64,500	3.12	185	10
PHBV + 0.5 wt% NA1	70.13	92.73	92,370	2.37	185	10
PHBV + 0.5 wt % NA2	46.45	63.68	96,400	2.62	185	10
PHBV + 0.5wt% NA 3	87.83	103.17	72,800	3.46	185	10
PHBV + 0.5 wt% NA5			13,400	3.66	185	10

When NA5 was used, the polymer was strongly degraded and only polymer of very low molecular mass (Mn) was obtained. The crystallization onset could not be determined.

Addition of NA1 increases the crystallization onset temperature of the polymer and results not in a decreased molar mass of the crystallized polymer.

NA2 neither decreases the molar mass polymer but the crystallization onset temperature is only increased marginally.

NA3 increases the crystallization onset temperature but the molar mass of the polymer is lower compared to the sample where the nucleating agent according to the invention (NA1) is used. The results show that the nucleating agent of current invention results in a good combination of properties: the onset crystallization temperature of the polymer is increased and the crystallized polymer retains a high molar mass.

Example 3 – Comparison of a nucleating agent according to the invention and known nucleating agents for the crystallization of PP

The crystallization behavior and the transparency of the obtained crystallized polymer were determined.

NA4 (known from EP2319882) comprises four urethane motifs and alkyl side arms. The results are shown in table 4.

.

Table 4 Crystallization of poly(propylene-ethylene) copolymer (PP) with different nucleating agents

Sample	T_C /T_c^N (°C)	T_{onset} (°C)	ΔH_c (J/g)	T_m (°C)	Process. Temp. (°C)	Cooling Rate (°C/min)	Transparency (% at 500 nm^{-1})
PP	91.9	97.8	81.4	142.2	230	10	7.74
PP + 0.3wt% NA1	101.8	108.9	87.8	142.3	230	10	8.11
PP + 0.5wt % NA2	105.33	107.06	103.8	141.7	230	10	3.11
PP + 0.5 wt% NA4	101.02	104.99	96.53	141.9	230	10	7.80
PP + 0.5 wt% NA5	114.55	118.95	107.9	144.3	230	10	0.61

The results show that the nucleating agent of the invention effectively increases the onset crystallization temperature and also the crystallization enthalpy. While the known nucleating agents also increase the onset crystallization temperature and the enthalpy, these nucleating agents result in a much lower transparency of the obtained polymer. NA1 increases the transparency of the polymer, while the other nucleating agents decrease the transparency of the polymer.

In the comparison, NA1 shows a good combination of properties: the transparency of the polymer is improved and the crystallization behavior is also improved.

The results of the comparison experiments of examples 2 and 3 demonstrate that the nucleating agents of present invention combine attractive properties.
They work effectively in the crystallization of a range of polymers, and obtained crystallized polymers have a good transparency and retain a high molar mass. Known nucleating agents may perform well for one of these criteria's but do not show the combination of properties.
Brief description of the drawing

Fig. 1: optical micrographs of crystallization of polypropylene copolymer including NA1 (top panel, described as “NA a”) or no nucleating agent (Ref., lower panel). Below each micrograph the time is indicated (s=seconds) at which the micrograph was taken, where 0 s indicates the time when the melt had reached a temperature of 120°C.

Nucleating agents for polyesters and polyolefins

Claims:

1) Use of at least one compound for crystallization of polyester or polyolefin polymers, characterized in that the compound comprises a core and side arms R and R' flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif;
wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:
(i) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;
(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;
(iii) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:
  (i) an alkyl group comprising 1 to 8 carbon atoms,
  (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,
  (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,
  (iv) a halogen or oxygen,
  (v) a monovalent functional group; or
(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;
and wherein the side arms R and R' are independently of each other chosen from:
(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;
(iii) one of the following esters:
- X-Ester-Y,
- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

2) The use of least one compound according to claim 1 wherein the side arms R and R' are the same.

3) The use of at least one compounds according to claim 1 or 2 wherein the compound has a peak melting temperature ranging between 100 and 300°C, preferably between 120 and 290°C, more preferably 150 and 280°C.

4) The use of at least one compound according to any one of claims 1-3 wherein the compound is applied at a concentration of 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% based on the weight of the polymer.

5) A process for crystallization of polyester or polyolefin polymer comprising the steps of:
(a) mixing the polymer with at least one compound at a first temperature, ranging from 10°C to 140°C above the peak melting temperature of the polymer; and
(b) cooling the polymer to a second temperature, ranging from the first temperature to 20°C,

characterized in that the compound comprises a core and side arms R and R' flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif;

wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:

(i) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;

(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;

(iii) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:

    (i) an alkyl group comprising 1 to 8 carbon atoms,

    (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,

    (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,

    (iv) a halogen or oxygen,

    (v) a monovalent functional group; or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;

and wherein the side arms R and R' are independently of each other chosen from:

(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;

(iii) one of the following esters:

- X-Ester-Y,
- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,

- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein

X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

6) The process according to claim 5, wherein the compound has a peak melting temperature ranging between between 100 and 300°C, preferably between 120 and 290°C, more preferably 150 and 280°C.

7) The process according to claim 5 or 6, wherein the compound is applied at a concentration of 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% based on the weight of the polymer.

8) The process according to any one of claims 5-7, wherein the first temperature ranges between 10°C and 140°C, preferably between 20°C and 120°C, more preferably between 40°C and 120°C above the peak melting temperature of the polymer.

9) The process according to any one of claims 5-8, wherein the second temperature ranges from 140°C above the peak melting temperature of the polymer to 20°C, preferably from 120°C above the peak melting temperature of the polymer to 20°C.

10) The process according to any one of claims 5-9, wherein the cooling occurs at a rate ranging between 1°C /min and 500°C /min, preferably between 10°C /min and 300°C /min, more preferably between 20°C /min and 100°C /min.

11) A composition comprising polyester or polyolefin polymer and at least one compound

characterized in that the compound comprises a core and side arms R and R' flanking the core, which core consists of two hydrogen bonding motifs and a linker connecting said hydrogen bonding motifs, wherein the hydrogen bonding motifs are independently of each other chosen from an amide motif, an oxalamide motif, a hydrazide motif, an urethane motif or an urea motif;

wherein the linker does not comprise any of said hydrogen bonding motifs and is chosen from:

(i) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one of the carbon atoms is substituted by a moiety comprising N, O, P or S;

(ii) an unsaturated aliphatic hydrocarbon group comprising 1 to 12 carbon atoms;

(iii) an alkanediyl group comprising 1 to 12 carbon atoms wherein at least one hydrogen atom is substituted by one of the following:

  (i) an alkyl group comprising 1 to 8 carbon atoms,

  (ii) an alkyl group comprising 1 to 8 carbon atoms, where one or more carbon atoms are substituted with heteroatoms or divalent organic functional groups,

  (iii) an alkyl group comprising 1 to 8 carbon atoms, where one or more hydrogen atoms are substituted with a halogen or a monovalent, organic functional group,

  (iv) a halogen or oxygen,

  (v) a monovalent functional group; or

(iv) an alkanediyl group comprising 1 to 5 carbon atoms if different hydrogen bonding motifs are connected by the linker;

and wherein the side arms R and R' are independently of each other chosen from:

(i) H;

(ii) an alkyl group with a total number of carbon atoms between 1 and 20;

(iii) one of the following esters:

- X-Ester-Y,
- X-Ester- X-Ester-Y,

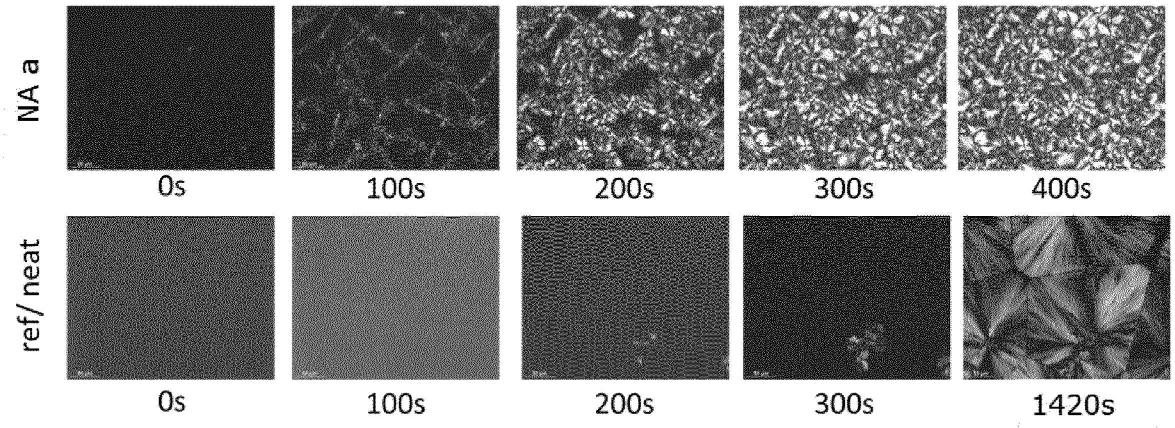
- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-Y,
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-Y, or
- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester- X-Ester-X-Ester-X-Ester-Y, wherein X is a saturated aliphatic hydrocarbon group comprising 1 to 20 carbon atoms, Y is chosen from H or an alkyl group with a total number of carbon atoms between 1 and 20 and Ester is –C(O)-O- or –O-C(O)-.

each hydrogen bonding motif resides in a molecular plane and wherein the linker between the hydrogen bonding motifs is chosen such that one of the hydrogen bonding motifs resides in a different molecular structural plane than the other hydrogen bonding motif(s).

12) The composition according to claim 11, wherein the compound or a combination of compounds is applied at a concentration of 0.05-2wt%, preferably 0.1-1wt%, more preferably 0.2-0.5wt% based on the weight of the polymer.

13) A film, molding, composite material, extrusion- or injection-molded product or elongated product comprising the composition according to claim 11 or 12.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/066897

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/20
ADD. C08L23/02 C08L67/00

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)
C08K C08L

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.
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X,P	WO 2013/156565 A1 (UNIV EINDHOVEN TECH [NL]) 24 October 2013 (2013-10-24) page 3, paragraph 3 - page 11, paragraph 3 page 19, paragraph 2; claims; examples -----	1-13
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 21 October 2014	Date of mailing of the international search report 29/10/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Engel, Hermann

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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