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(54) Title: PROCESS FOR THE COPOLYMERISATION OF  $\alpha$ -OLEFINS WITH VINYL MONOMERS

(57) Abstract: The invention involves a process for the copolymerisation of at least one ( $\alpha$ -olefin with at least one vinyl monomer containing at least one hetero atom chosen from the group consisting of Si, O, N, and halogen, and/or at least one optionally substituted aryl group, which vinyl monomer is homopolymerizable via ATRP ("vinyl monomer A"), wherein the copolymerisation is performed in the presence of at least one transition metal compound which comprises a low valent transition metal which can undergo one-electron oxidation, and a ligand which is capable of coordinating in a  $\sigma$ -bond and/or a  $\pi$ -bond to the transition metal, and at least one co-compound with formula RX, in which R represents a substituted, activated alkyl group or a arylsulphonyl group, and X represents a halogen, and in which the molar ratio RX : ( $\alpha$ -olefin + vinyl monomer A) is between 1:5 and 1:1000. The invention also involves a copolymer comprising at least one  $\alpha$ -olefin and at least one vinyl monomer A, the copolymer having an  $M_w/M_n$  smaller than 1.5.

PROCESS FOR THE COPOLYMERISATION OF  $\alpha$ -OLEFINS WITH VINYL  
MONOMERS

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The invention relates to a process for the copolymerisation of at least one  $\alpha$ -olefin with at least one vinyl monomer containing at least one hetero atom chosen from the group consisting of Si, O, N, and halogen, and/or at least one optionally substituted aryl group, which vinyl monomer (hereinafter abbreviated as "vinyl monomer A") is homopolymerizable via atom transfer radical polymerization (ATRP). The invention also relates to a copolymer comprising at least one  $\alpha$ -olefin and at least one vinyl monomer A.

Copolymers of an  $\alpha$ -olefin with for example a polar vinyl monomer, having various architectures remain an ultimate goal in polyolefin engineering. Since, of the many permutations available for modifying the properties of polyolefins, the incorporation of functional groups into an otherwise nonpolar material is substantial. Polar groups exercise control over important properties such as toughness, adhesion, barrier properties, surface properties, for example paintability and printability, solvent resistance, miscibility with other polymers, and rheological properties. In order to realise structurally well-defined linear copolymers comprised of nonpolar and polar monomer units by the copolymerisation of two or more monomers, the amount of the monomers in the copolymer and distribution of comonomer in the copolymer must be controllable. Aside from monomer concentration, the other important determinant in this process is the relative reactivity of the monomers.

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The copolymerisation of  $\alpha$ -olefins, i.e. ethylene, 1-hexene and norbornene with methacrylate in the presence of a neutral palladium pyrrole-imine complex is disclosed in G. Tian et al., *Macromolecules*, **34** (2001), p. 7656.

A drawback of the known process is, that is the resulting copolymers have a relatively broad molecular weight distribution, defined as  $M_w/M_n$ , wherein  $M_w$  is the weight average molecular weight and  $M_n$  is the number average molecular weight, both determined with size exclusion chromatography (SEC). The  $M_w/M_n$  of such polymers is usually larger than 1.5.

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The aim of the present invention is to provide a process for the copolymerisation of at least one  $\alpha$ -olefin with at least one vinyl monomer A, the process resulting in a copolymer having a narrow MWD.

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Surprisingly, this is achieved according to the present invention by performing the copolymerisation in the presence of at least one transition metal compound which comprises a low valent transition metal which can undergo one-electron oxidation and a ligand which is capable of coordinating in a  $\sigma$ -bond and/or a  $\pi$ -bond to the transition metal, and at least one co-compound with formula RX, in which R represents a substituted activated alkyl group or an arylsulphonyl group, and X represents a halogen, and in which the molar ratio RX: ( $\alpha$ -olefin + vinyl monomer A) is between 1:5 and 1:1000.

By the process according to the invention copolymers with a relatively narrow MWD can be obtained, the  $M_w/M_n$  being smaller than 1.5, typically being between 1.0 and 1.3, as determined by Size Exclusion Chromatography (SEC). Further advantages of the process according to the invention are that relatively large amounts of the vinyl monomer A can be incorporated at a reasonably high  $\alpha$ -olefin : vinyl monomer A molar ratio. Furthermore, copolymers may be produced with a relatively narrow chemical composition distribution (CCD). Attractive overall rates of polymerization can be obtained, and, finally, the process is a living polymerization process and thus makes it possible to control the comonomer distribution in order to produce tailor-made polymers, for example block copolymers.

The transition metal compound according to the present invention comprises one or more low valent transition metal ions. Within the scope of the present invention low valent transition metal ions are understood to be transition metal ions which are not in their highest possible oxidation state and, as such, can undergo one-electron oxidation. The possible oxidation states of transition metals are commonly known in the art, for example from "Advanced Inorganic Chemistry", F.A. Cotton and G. Wilkinson, John Wiley & Sons, 5<sup>th</sup> ed., 1988, p. 625-954. Suitable low valent transition metal ions are mentioned in M. Kamigaito et al., Chem. Rev., 101 (2001), 3689-3745, and in K. Matujaszewski et al., Chem. Rev., 101 (2001) (p. 2935-2940), which publications are incorporated herein by reference, Preferably the low valent transition metal ion is chosen from the group comprising Cu(I), Ru(I), Ni(II), Fe(II), Pd(II), Rh(II), Re(V) and Mo(V). More preferably the low valent transition metal ion is Cu(I).

In addition to the low valent transition metal ion, one or more transition metals with a higher valency may also be present in the reaction mixture. For example, when Cu(I) is used as the low valent transition metal ion, Cu(II) may also be

employed in order to suppress a radical termination reaction, as a result of which better control of the copolymerization process is obtained.

The transition metal compound according to the present invention further comprises one or more ligands which are capable of coordinating to the transition metal in a  $\sigma$ -bond and/or a  $\pi$ -bond. The term "ligand" and the terms " $\sigma$ -bond" and " $\pi$ -bond" are commonly known in the art, and defined in for example "Advanced Inorganic Chemistry", F.A. Cotton and G. Wilkinson, John Wiley & Sons, 5<sup>th</sup> ed., 1988, p. 35-36. Suitable ligands which can be used in the process according to the invention are for example N- or S-containing ligands, which can coordinate to the transition metal ion via at least one N and S hetero atom, respectively. Preferably, an N-containing ligand is used. Suitable N-containing ligands are mentioned in M. Kamigaito et al., Chem. Rev., 101 (2001), 3689-3745 (Figure 8, p. 3701), and in K. Matujaszewski et al., Chem. Rev., 101 (2001) (p. 2941-2942), which publications are incorporated herein by reference, and include for example optionally substituted bi- or tridentate pyridine based ligands (for instance optionally substituted bipyridines), optionally substituted linear, aliphatic, multidentate amine ligands (for instance N,N,N',N'',N'''-pentamethyldiethylenetriamine) and optionally substituted cyclic aza compounds (for instance 1,4,8,11-tetramethyl-1,4,9,11-tetraazacyclotetradecane). If Cu(I) is used as the transition metal ion, preferably a linear, aliphatic, multidentate amine ligand is used.

The transition metal compound may further comprise one or more counter ions. The number of said counter ions depends on the valency of the transition metal ion, the number and charge of charged ligands (if present), and the charge of the counter ion. Examples of suitable counter ions are halogens (for example chloride and bromide), pseudohalides (for example thiocyanide), triflate, and carboxylates (for example acetates). Some counter ions may also act as a ligand, for example 2-thiophenecarboxylate, 8-oxyquinoline, mono- and multi-substituted picolinates and thiocyanates.

The transition metal : ligand and transition metal : counter ion molar ratios may vary within broad ranges, and will usually lie between 5:1 and 1:5 for the transition metal ion : ligand ratio, and 2:1 and 1:4 for the transition metal ion : counter ion ratio.

In the compound with formula RX, R represents a substituted activated alkyl group or an arylsulphonyl group. In the context of the present invention, a substituted activated alkyl group is an alkyl group which contains on its  $\alpha$ -carbon

atom, i.e. the carbon atom directed bound to X, at least one substituent chosen from the group comprising CN, C(O)R, C(O)OR, phenyl, and halogen (preferably Cl). Alternatively, a substituted activated alkyl group is an alkyl group which contains on its  $\alpha$ -carbon atom 2 or 3 alkyl substituents of which at least one alkyl substituent is a methyl group. X preferably is Cl or Br, more preferably Br. Examples of RX are mentioned in M. Kamigaito et al., Chem. Rev., 101 (2001), 3689-3745 (Figure 8, p. 3701), and in K. Matujaszewski et al., Chem. Rev., 101 (2001) (p. 2932-2935), which publications are incorporated herein by reference. Preferably ethyl-2-bromoisobutyrate, tetrachloromethane, trichloro acetic acid or trichloro ethanol are used.

10 The process according to the invention involves the copolymerisation of at least one  $\alpha$ -olefin with at least one vinyl monomer A.

Herein an  $\alpha$ -olefin is defined as a compound with formula  $\text{CH}_2=\text{CH}-\text{R}'$ , in which R' represents for example a linear or branched (hetero)alkyl with for example 1-24 carbon atoms, which is optionally substituted with one or more substituents which are inert under the chosen reaction conditions. Suitable examples of such substituents are a hydroxy group, an amine group, an amide group, a thiol group, a halogen, an alkoxy group with for example 1 to 20 C atoms, a (hetero)aryl group with for example 1 to 20 C atoms and an aryloxy group with for example 1 to 20 C atoms. Preferably R' represents an unsubstituted linear alkyl with 1-10 carbon atoms, more preferably an unsubstituted linear alkyl with 2-6 carbon atoms.

As the vinyl monomer A, monomers can be used which contain substituents that can stabilize the propagating radicals during the copolymerization reaction. Examples of vinyl monomer A are mentioned in M. Kamigaito et al., Chem. Rev., 101 (2001), 3689-3745 (Figure 11, p. 3706), and in K. Matujaszewski et al., Chem. Rev., 101 (2001) (p. 2928-2932), which publications are incorporated herein by reference. Preferably an acrylate, a methacrylate, a styrene, an acrylonitrile, a vinyl pyridine, a (meth)acrylamide, or a maleimide is used as the vinyl monomer A.

The total monomer concentration, i.e. [ $\alpha$ -olefin + vinyl monomer A], may vary between broad ranges and depends on e.g. the type of monomers used. Usually the total monomer concentration is between 1 mol/l and bulk, preferably between 3 and 8 mol/l.

The molar ratio  $\alpha$ -olefin : vinyl monomer A is dependent on e.g. the desired amounts of each of the comonomers in the copolymer and is usually between 5:95 and 75:25, preferably between 25:75 and 50:50.

The molar ratio RX : ( $\alpha$ -olefin + vinyl monomer A) determines, among other reaction parameters (such as the temperature), the molecular weight of the product, and, in order to obtain a reasonable molecular weight, must be between 1:5 and 1:1000, preferably between 1:7 and 1:500, more preferably between 1:10 and 1:100.

The molar ratio transition metal compound : RX is usually smaller than 2:1, preferably smaller than 1:1, more preferably between 0.5:1 and 1:1.

The process according to the invention may be carried out in solution or in bulk. For solution processes, non-polar or less-polar solvents are preferred, for example aromatic hydrocarbons, for example optionally substituted benzene, toluene or xylene. However, more polar solvents, for example ketones (for example acetone), esters (for example ethylene carbonate), ethers (for example diphenyl ether, tetrahydrofuran), and N,N-dimethylformamide may also be employed. In fact, due to the radical nature of the copolymerization reaction, even protic solvents such as alcohols and water can be employed.

The process is preferably carried out at a reaction temperature between 20 and 150 °C, more preferably between 80 and 120 °C. At temperatures lower than 20 °C the reaction will be relatively slow and the reactants could be badly soluble, while at temperatures higher than 150 °C the number of side reaction increase, resulting in a broader MWD.

The pressure at which the process according to the invention is carried out is not particularly critical and depends on for example the monomers, the solvent and the reaction temperature. When higher  $\alpha$ -olefins are applied, for practical reasons the process is preferably carried out at atmospheric pressure.

The reaction time is not particularly critical and is dependent on for example the types and amounts of the transition metal compound, RX, and comonomers used, the temperature and the solvent. Usually a reaction time of at least 1 hour to 4 days is applied, more preferably a reaction time between 2 and 48 hours, most preferably a reaction time between 3 and 24 hours.

Polymerisation conditions similar to those described for the process according to the present invention are disclosed in for example WO96/30421, wherein a polymerisation process based on transition metal-mediated ATRP is described. In the above mentioned patent application, however, the (co)polymerisation of an  $\alpha$ -olefins with a vinyl monomer A is not disclosed. In fact,  $\alpha$ -olefins are commonly known to

undergo degradative chain transfer of allylic hydrogen atoms when involved in free radical reactions. The stable radicals derived from the  $\alpha$ -olefin monomer after such chain transfer reactions are slow to reinitiate and prone to terminate. It could therefore not be expected that  $\alpha$ -olefins could be copolymerised with vinyl monomers A by using  
5 the method according to the present invention.

The invention also relates to a copolymer comprising at least one  $\alpha$ -olefin and at least one vinyl monomer A. Such copolymers are disclosed in for example G. Tian et al., *Macromolecules*, 34 (2001), p. 7656.

A drawback of the known copolymers is, that they have a relatively  
10 large  $M_w/M_n$ .

The aim of the present invention is to provide a copolymer of an  $\alpha$ -olefin and a vinyl monomer A with a small  $M_w/M_n$ .

The invention surprisingly provides a new copolymer of an  $\alpha$ -olefin and a vinyl monomer A having an  $M_w/M_n$  smaller than 1.5. Such a polymer is for  
15 example obtainable by using the process according to the invention.

The  $M_n$  of the copolymer according to the invention can vary within broad ranges and is preferably between 500 and 200,000 g/mol, more preferably between 800 and 100,000 g/mol, most preferably between 1000 and 75,000 g/mol. The amount of  $\alpha$ -olefin and vinyl monomer A in the copolymer according to the invention  
20 may also vary within broad ranges, the  $\alpha$ -olefin : vinyl monomer A molar ratio in the copolymer preferably being between 90:10 and 10:90, more preferably between 80:20 and 20:80, and most preferably between 50:50 and 25:75. Both the  $M_n$  and the  $\alpha$ -olefin : vinyl monomer A molar ratio can be chosen to fit the requirements of the application in which the copolymer according to the invention is used. This can be done  
25 in the process according to the invention for example by using the RX : ( $\alpha$ -olefin + vinyl monomer A) molar ratio to control the  $M_n$ , and by using the  $\alpha$ -olefin : vinyl monomer A molar ratio in the feed to control the  $\alpha$ -olefin : vinyl monomer molar ratio in the copolymer according to the invention.

The copolymerization according to the invention is a living  
30 copolymerization, i.e. a copolymerization in which the copolymer chains grow simultaneously throughout the reaction. One of the implications of this copolymerization mechanism is that, in contrast to conventional free radical polymerization, in which the copolymer chains grow sequentially, the chemical composition of the polymer chains will all be similar, while the chemical composition in each chain may vary significantly

over the position on the copolymer chain. In general, however, the distribution of the  $\alpha$ -olefin over the copolymer chain will be relatively narrow.

The invention also relates to the use of the copolymer according to the invention in coating compositions.

5                   In the automotive industry, polymers, preferably polyolefins, and more preferably polypropylene or its copolymers, are used in bumpers and other exterior parts. Said polymers are usually coated with a coating composition. As such coating compositions are usually relatively polar, they are generally not sufficiently compatible with the non-polar polypropylene and its (co)polymers. Therefore, parts made of  
10 polypropylene or its copolymers are usually subjected to some form of pre-treatment before coating to increase their polarity.

The problem of the known method is that such a pretreatment step is necessary.

15                   It has now surprisingly been found that such pre-treatment can be obviated by using a coating composition comprising the copolymer according to the present invention. As the copolymer according to the invention contains an  $\alpha$ -olefin, it will be compatible with parts made of polypropylene and its copolymers. Hence, pre-treatment of these plastic parts would not be required, which in turn would lead to massive cost savings and improved quality of the coating of these parts.

20                   On the other hand, the copolymer according to the invention can also be used in coating compositions for the coating of polar substrates. By using a copolymer according to the invention, which contains both an  $\alpha$ -olefin and a polar vinyl monomer A, a good adhesion to e.g. metal surfaces can be obtained due to the presence of the polar groups in the copolymer. At the same time, a coating composition  
25 containing a copolymer according to the present invention may offer good protective properties due to the low surface energy of the  $\alpha$ -olefin part of the copolymer. Examples of copolymers suitable for the use in coating compositions are copolymers of  $\alpha$ -olefins with methyl (meth)acrylate, glycidyl (meth) acrylate, hydroxyethyl (meth)acrylate, and styrene.

30                   The invention further relates to the use of the copolymer according to the invention as a compatibilizer.

The copolymer according to the present invention can be used for example as a compatibilizer in polymer blends comprising one or more relatively polar (co)polymers, for example poly(methylmethacrylate), polyacrylate, styrene maleic



anhydride copolymer, and polystyrene, and one or more relatively apolar (co)polymers, for example polypropylene and polyethylene. Such blends are for example used to combine the positive properties of the relatively polar (co)polymer(s), for example hardness, scratch resistance, chemical resistance, dimensional stability, and heat  
5 resistance, with the positive properties of the relatively apolar (co)polymer(s), for example tensile strength, low density, and relatively low cost price.

Said copolymer can also be used as a tie resin in multi-layer films, offering the possibility to combine the barrier properties of at least two films, for example of a film comprising one or more relatively apolar (co)polymer(s), for example  
10 polypropylene and/or polyethylene, and a film comprising one or more relatively polar (co)polymers, for example ethene-vinyl alcohol copolymer.

The invention is further illustrated by the following non-limiting Examples and comparative experiments.

## 15 Examples

### Starting materials

Methyl acrylate ("MA", Aldrich, 99+%), methyl methacrylate ("MMA", Aldrich, 99%), butyl acrylate ("BA", Aldrich, 99+%), styrene ("STY", Aldrich, 99+%),  
20 1-hexene (Aldrich, 99+%), and 1-octene (Aldrich, 98%) were distilled and stored over molecular sieves.

*p*-Xylene (Aldrich, 99+% HPLC grade) was stored over molecular sieves and used without further purification. N,N,N',N',N"-pentamethyldiethylene triamine ("PMDETA", Aldrich, 99%), ethyl-2-bromoisobutyrate (Aldrich, 98%), CuBr  
25 (Aldrich, 98%), CuBr<sub>2</sub> (Aldrich, 98%), aluminium oxide (activated, basic, for column chromatography, 50-200 μm), tetrahydrofuran ("THF", Aldrich, Analytical Reagent), 1,4-dioxane (Aldrich, AR), and dimethyl formamide ("DMF", Aldrich, AR) were all used as received.

## 30 Copolymerizations

A typical copolymerization of 1-octene and MA was carried out as follows: to a 100 ml three-neck round-bottom flask, PMDETA (0.29 g, 1.67 × 10<sup>-3</sup> mol) was added as a ligand to a solution of *p*-xylene (23.2 g, 2.2 × 10<sup>-1</sup> mol), MA (4.67 g, 5.4 × 10<sup>-2</sup> mol) and 1-octene (6.1 g, 5.4 × 10<sup>-2</sup> mol) (MA : 1-octene molar ratio being 50 :

50). Subsequently, CuBr (0.19 g,  $1.3 \times 10^{-3}$  mol) and CuBr<sub>2</sub> (0.07 g,  $3.3 \times 10^{-4}$  mol) were added. After the mixture was stirred and bubbled with argon for 30 min, the flask was immersed in a thermostated oil bath kept at 80 °C and stirred for 10 min. A light green, slightly heterogeneous system was obtained. The co-compound RX, ethyl-2-bromoisobutyrate (0.65 g,  $0.3 \times 10^{-3}$  mol), was added slowly via a degassed syringe. The preparations were carried out under a flowing argon atmosphere. Samples were withdrawn at suitable time periods throughout the polymerization. A pre-determined amount of the sample was transferred immediately after withdrawing into a gas chromatography (GC) vial and diluted with 1,4-dioxane or THF, so as to determine the monomer conversion using GC. The remaining sample was diluted with THF, passed through a column of basic alumina prior to SEC and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements.

A typical copolymerization of 1-octene and MMA was carried out in a similar way, by adding PMDETA (0.07 g,  $4 \times 10^{-4}$  mol) to a solution of *p*-xylene (11.1 g,  $1.0 \times 10^{-1}$  mol), MMA (2.4 g,  $2.4 \times 10^{-2}$  mol) and 1-octene (2.7 g,  $2.4 \times 10^{-2}$  mol) (MMA : 1-octene molar ratio being 50 : 50). Subsequently, CuCl (0.038 g,  $3.8 \times 10^{-4}$  mol) and CuCl<sub>2</sub> (0.0027 g,  $2.0 \times 10^{-5}$  mol) were added. The above polymerization procedure was applied. Trichloroethanol (0.15 g,  $1.0 \times 10^{-3}$  mol) was used as RX.

A typical copolymerization of 1-hexene and BA was carried out in a similar way, by adding PMDETA (0.29 g,  $1.67 \times 10^{-3}$  mol) to a solution of *p*-xylene (16.3 g,  $1.5 \times 10^{-1}$  mol), BA (8.4 g,  $6.6 \times 10^{-2}$  mol) and 1-hexene (0.61 g,  $7.3 \times 10^{-3}$  mol) (BA : 1-hexene molar ratio being 90 : 10). Subsequently, CuBr (0.19 g,  $1.3 \times 10^{-3}$  mol) and CuBr<sub>2</sub> (0.07 g,  $3.3 \times 10^{-4}$  mol) were added. The above polymerization procedure was applied. Ethyl-2-bromoisobutyrate (0.65 g,  $3.3 \times 10^{-3}$  mol) was used as RX.

A typical copolymerization of 1-octene and styrene was carried out in a similar way, by adding PMDETA (0.14 g,  $8.3 \times 10^{-4}$  mol) to a solution of *p*-xylene (7.3 g,  $6.9 \times 10^{-2}$  mol), styrene (3.5 g,  $3.4 \times 10^{-2}$  mol) and 1-octene (1.3 g,  $1.1 \times 10^{-2}$  mol) (styrene : 1-octene molar ratio being 75 : 25). Subsequently, CuBr (0.12 g,  $8.3 \times 10^{-4}$  mol) was added. The above polymerization procedure was applied. Ethyl-2-bromoisobutyrate (0.33 g,  $1.7 \times 10^{-3}$  mol) was used as RX.

The amounts of the starting materials may vary. For example, the amount of RX is chosen in function of the targeted molecular weight.

### Analysis

Monomer conversion was determined from the concentration of the residual monomer using a Hewlett-Packard (HP-5890) GC, equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 μm); DMF was used as the internal reference.

5 In some cases the solvent (p-xylene) was used as the reference.

Molar mass and molar mass distributions were measured by SEC, at ambient temperature using a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 mL/min. A set of two linear columns (Mixed-C, Polymer Laboratories, 10 30 cm, 40 °C) was used. Calibration was carried out using narrow polydispersity polystyrene ("PS") standards ranging from 600 to 7 × 10<sup>6</sup> g/mol and molar masses were calculated using the universal calibration principle and Mark-Houwink parameters (PMA: K = 1.95 × 10<sup>-4</sup> dL/g, a = 0.660). Data acquisition and processing were performed using Waters Millenium 32 software.

15 MALDI-TOF MS measurements were performed to determine the polymer composition on a Voyager-D(elayed) E(xtraction) STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. Positive-ion spectra were acquired in reflector mode. Dithranol was chosen as the matrix.

### 20 Examples I-III. Copolymerization of 1-hexene or 1-octene with MA or BA

Reaction conditions applied in Examples I-III are given in Table 1. The mol% of monomer given are relative to the total amount of monomers, e.g. (α-olefin + vinyl monomer A). The results of the polymerization reactions are given in Table 2.

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Table 1: Examples I-V; reaction conditions

Example	1-Hexene (mol%)	1-Octene (mol%)	MA (mol%)	BA (mol%)	Reaction temperature (°C)	Reaction time (h)
I	10	0	0	90	70	16
II	0	25	75	0	80	22
III	10	0	90	0	65	10

Table 2: Results Examples I-III

Example	Comonomer conversion (%)			Comonomer in copolymer (mol%)			M <sub>n</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
	1-hexene (Ex. II : 1-octene)	MA	BA	1-hexene (Ex. II: 1-octene)	MA	BA		
I	37	-	93	4.2	0	96	4315	1.2
II	33	95	-	10.4	90	0	2404	1.3
III	20	46	-	4.8	95	0	1604	1.1

5 Examples IV-VII: Copolymerization of 1-octene with MA, MMA or styrene

Reaction conditions applied in Examples IV-VII are given in Table 3.

The results of the polymerization reactions are given in Table 4.

Table 3: Examples VI-IX; reaction conditions

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Example	1-Octene (mol%)	MA (mol%)	MMA (mol%)	Styrene (mol%)	Reaction temperature (°C)	Reaction time (h)
IV	25	75	-	-	80	48
V	50	50	-	-	80	48
VI	50	-	50	-	90	25
VII	25	-	-	75	110	12

Table 4: Examples IV-VII; Results

Example	Comonomer content in copolymer (mol%)				M <sub>n</sub> copolymer (g/mol)	M <sub>w</sub> /M <sub>n</sub> copolymer
	1-Octene	MA	MMA	STY		
IV	14	86	-	-	2465	1.3
V	23	77	-	-	1950	1.3
VI	19	-	81	-	2285	1.3
VII	16	-	-	84	1300	1.2

5 Comparative experiments A-D: Copolymerization of 1-octene with methyl acrylate, methyl methacrylate and styrene

A typical free radical polymerization (FRP) was carried out as follows:

To a 100 ml three-neck round-bottom flask, *p*-xylene (10.0 g,  $9.5 \times 10^{-2}$  mol), MA (3.5 g,  $4.1 \times 10^{-2}$  mol) and 1-octene (1.5 g,  $1.4 \times 10^{-2}$  mol) were added. After the reaction mixture was bubbled with argon for 30 min, the flask was immersed in a thermostated oil bath kept at 80 °C and stirred for 10 min. The initiator,  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) (0.025 g,  $1.0 \times 10^{-2}$  mol/l), dissolved in a minimum amount of *p*-xylene, was added slowly via a degassed syringe. The reactions were carried out under a flowing argon atmosphere. Samples were withdrawn at suitable time periods throughout the polymerization. A pre-determined amount of the sample was transferred immediately after withdrawing into a GC vial and diluted with 1,4-dioxane or THF, so as to determine the monomer conversion using GC. The remaining sample was diluted with THF, prior to SEC and MALDI-TOF-MS measurements.

20 Reaction conditions applied in comparative experiments A-D are given in Table 5. The results are given in Table 6.

Table 5: Comparative experiments A-D; reaction conditions

Comparative experiment	1-Octene (mol%)	MA (mol%)	MMA (mol%)	Styrene (mol%)	Reaction temperature (°C)	Reaction time (h)
A	25	75	0	0	80	48
B	50	50	0	0	80	48
C	25	0	75	0	80	7
D	25	0	0	75	110	6

5 Table 6: Comparative experiments A-D; Results

Comparative experiment	Comonomer content in copolymer (mol%)				Mn copolymer (g/mol)	Mw/Mn copolymer
	1-octene	MA	MMA	MA		
A	14	86	0	0	7707	3.7
B	26	75	0	0	5943	2.9
C	5.7	0	94	0	26139	1.6
D	16	0	0	84	22729	2.7

The results in Table 6 show that copolymers comprising an  $\alpha$ -olefin and a vinyl monomer A, produced by free-radical polymerization instead of ATRP, feature a broad MWD, the  $M_w/M_n$  being larger than 1.5.

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CLAIMS

1. Process for the copolymerisation of at least one  $\alpha$ -olefin with at least one vinyl monomer containing at least one hetero atom chosen from the group consisting of Si, O, N, and halogen, and/or at least one optionally substituted aryl group, which vinyl monomer ("vinyl monomer A") is homopolymerizable via atom transfer radical polymerization (ATRP), characterized in that the copolymerisation is performed in the presence of at least one transition metal compound which comprises a low valent transition metal which can undergo one-electron oxidation, and a ligand which is capable of coordinating in a  $\sigma$ -bond and/or a  $\pi$ -bond to the transition metal, and at least one co-compound with formula RX, in which R represents a substituted, activated alkyl group or a arylsulphonyl group, and X represents a halogen, and in which the molar ratio RX : ( $\alpha$ -olefin + vinyl monomer A) is between 1:5 and 1:1000.
2. Process according to claim 1 wherein the low valent transition metal is chosen from the group comprising Cu(I), Ru(I), Ni(II), Fe(II), Pd(II), Rh(II), Re(V) and Mo(V).
3. Process according to claim 2 wherein said low valent transition metal is Cu(I).
4. Process according to any one of claims 1-3, wherein the ligand is an N-containing ligand.
5. Process according to claim 4, wherein the ligand is a linear, aliphatic, multidentate amine ligand.
6. Process according to any one of claims 1-5, wherein RX is an alkyl bromide.
7. Process according to any one of claims 1-6, wherein the  $\alpha$ -olefin is a compound with formula  $\text{CH}_2=\text{CH-R}'$  in which R' represents an unsubstituted linear alkyl with 2-6 carbon atoms.
8. Process according to any one of claims 1-7, wherein the vinyl monomer A is chosen from the group comprising an acrylate, a methacrylate, a styrene, an acrylonitrile, a vinyl pyridine, an acrylamide, and a maleimide.
9. Process according to any one of claims 1-8, characterised in that the process further comprises the use of an aromatic hydrocarbon as a solvent.
10. Process according to any one of claims 1-9, characterised in that the molar ratio  $\alpha$ -olefin : vinyl monomer A is between 25:75 and 50:50.

11. Process according to any one of claims 1-10, characterised in that the molar ratio RX : ( $\alpha$ -olefin + vinyl monomer A) is between 1:10 and 1:100.
12. Process according to any one of claims 1-11, characterised in that the molar ratio transition metal compound : RX is between 0.5:1 and 1:1.
- 5 13. Process according to any one of claims 1-12, characterised in that the process is performed at a temperature between 70 and 120 °C.
14. Copolymer comprising at least one  $\alpha$ -olefin and at least one vinyl monomer ("vinyl monomer A"), characterised in that the copolymer has an  $M_w/M_n$  smaller than 1.5.
- 10 15. Copolymer according to claim 14, characterized in that the  $M_n$  of the copolymer is between 500 and 200,000 g/mol.
16. Copolymer according to claim 14 or claim 15, characterized in that the  $\alpha$ -olefin : vinyl monomer A molar ratio in the copolymer is between 90:10 and 10:90.
- 15 17. Copolymer comprising at least one  $\alpha$ -olefin and at least one vinyl monomer ("vinyl monomer A") obtainable by a process according to any one of claims 1-13.
18. Use of a copolymer according to any one of claims 14-17 in a coating composition.
- 20 19. Use of a copolymer according to any one of claims 14-17 as a polymer compatibilizer.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 03/00277

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F212/08

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)

IPC 7 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 practical, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 854 364 A (SENNINGER THIERRY ET AL) 29 December 1998 (1998-12-29) column 9, line 45 -column 9, line 67 column 10, line 26 -column 10, line 29; examples ---	1-5,7-9, 14-16
X	DAVIS KELLY A ET AL: "ABC triblock copolymers prepared using atom transfer radical polymerization techniques" MACROMOLECULES;MACROMOLECULES MAR 27 2001, vol. 34, no. 7, 27 March 2001 (2001-03-27), pages 2101-2107, XP002212147 examples ---	1-6,8, 10-16
X	US 5 807 937 A (MATYJASZEWSKI KRZYSZTOF ET AL) 15 September 1998 (1998-09-15) column 6, line 45 -column 6, line 61 ---	17,18
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*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.
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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 03/00277

C.(Continuation) 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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