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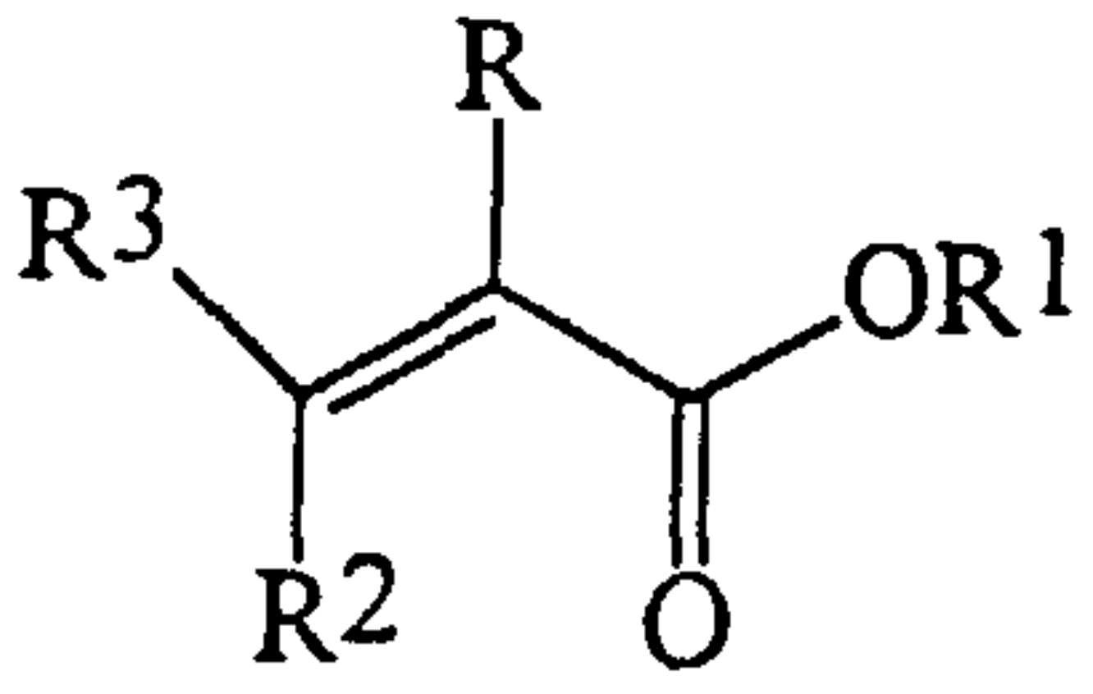
(54) **Titre :** COPOLYMERES A GRADIENT D'INDICE ET PROCEDE PERMETTANT DE LES PREPARATION ET LEUR UTILISATION

(54) **Title:** GRADIENT COPOLYMERS, AS WELL AS A METHOD FOR THEIR PREPARATION AND USE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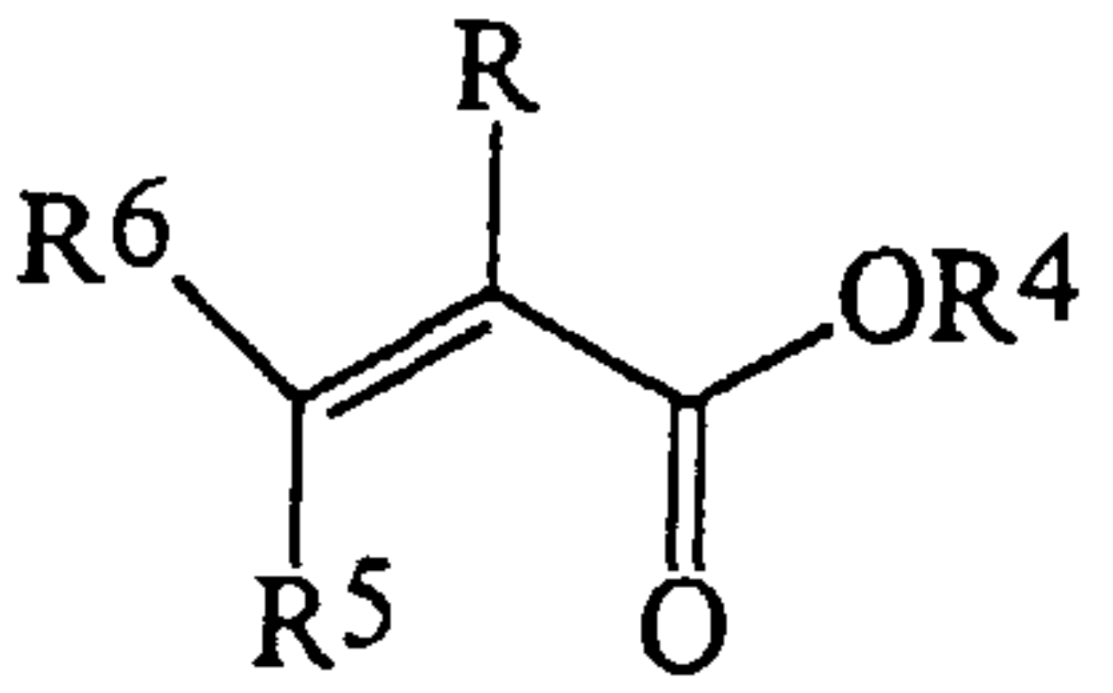
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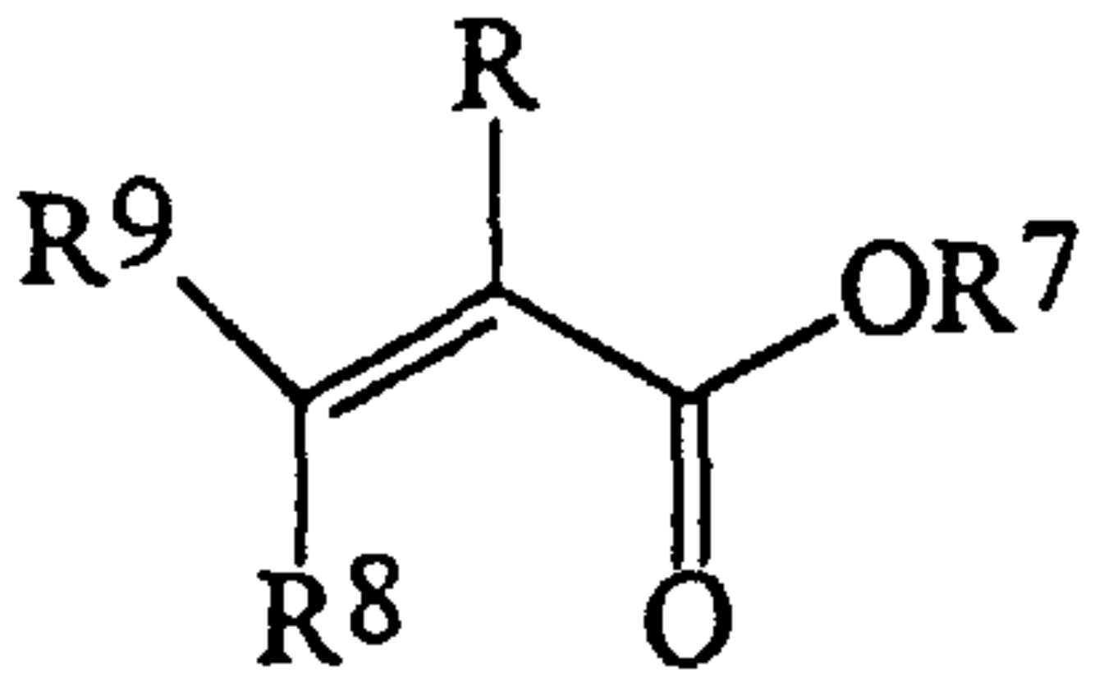
(III)

(57) **Abrégé/Abstract:**

The invention relates to gradient copolymers which can be obtained by polymerizing a mixture of olefinically unsaturated monomers. Said mixture is comprised of: a) 0 to 40 wt. % of one or more ethylenically unsaturated ester compounds of formula (I), wherein R represents hydrogen or methyl, R^1 represents a linear or branched alkyl radical with 1 to 5 carbon atoms, R^2 and R^3 independently represent hydrogen or a group of formula -COOR', wherein R' represents hydrogen or an alkyl group with 1 to 5 carbon atoms, of; b) 10 to 98 wt. % of one or more ethylenically unsaturated ester compounds of formula (II), wherein R represents hydrogen or methyl, R^4 represents a linear or branched alkyl radical with 6 to 15 carbon atoms, R^5 and R^6 independently represent hydrogen or a group of formula -COOR", wherein R" represents hydrogen or an alkyl group with 6 to 15 carbon atoms, of; c) 0 to 80 wt. % of one or more ethylenically unsaturated ester compounds of formula (III), wherein R represents hydrogen or methyl, R^7 represents a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9 independently represent hydrogen or a group of formula -COOR"', wherein R"' represents hydrogen or an alkyl group with 16 to 30 carbon atoms, and of; d) 0 to 50 wt. % of comonomers, whereby the mixture of the ethylenically unsaturated monomers is modified during chain growth in order to obtain copolymers, which have a gradient. The novel copolymers are used as setting point improvers.

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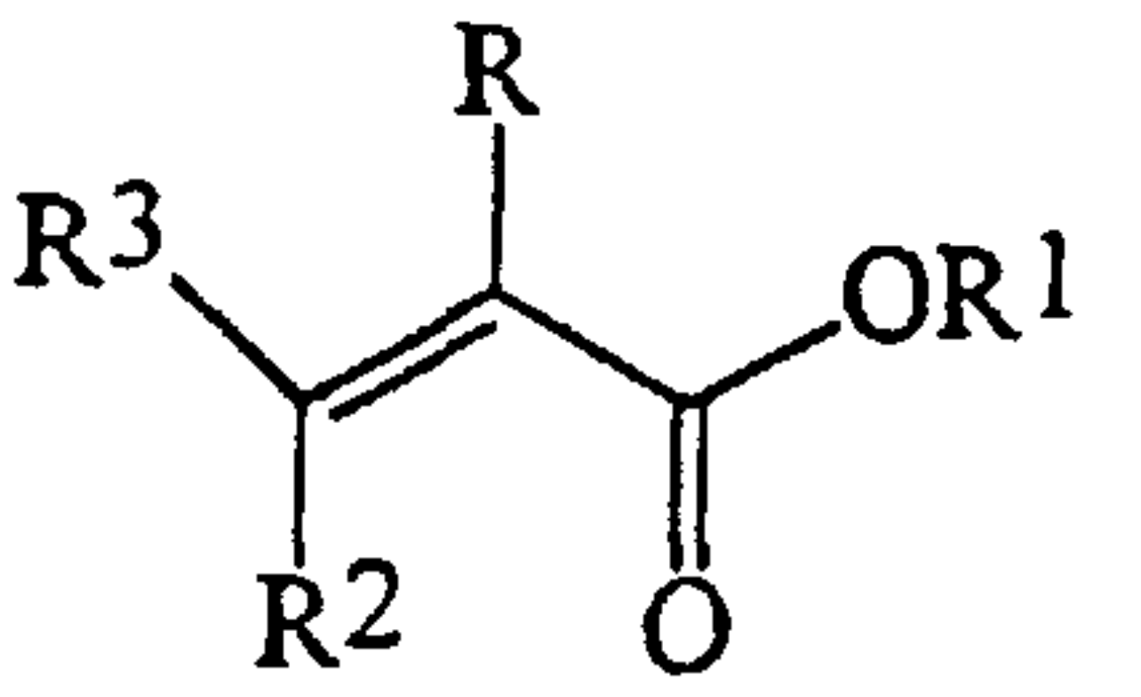
[Fortsetzung auf der nächsten Seite]

(54) Title: GRADIENT COPOLYMERS AND METHOD FOR THE PRODUCTION THEREOF AND THEIR USE

(54) Bezeichnung: GRADIENTENCOPOLYMERE SOWIE VERFAHREN ZUR HERSTELLUNG UND VERWENDUNG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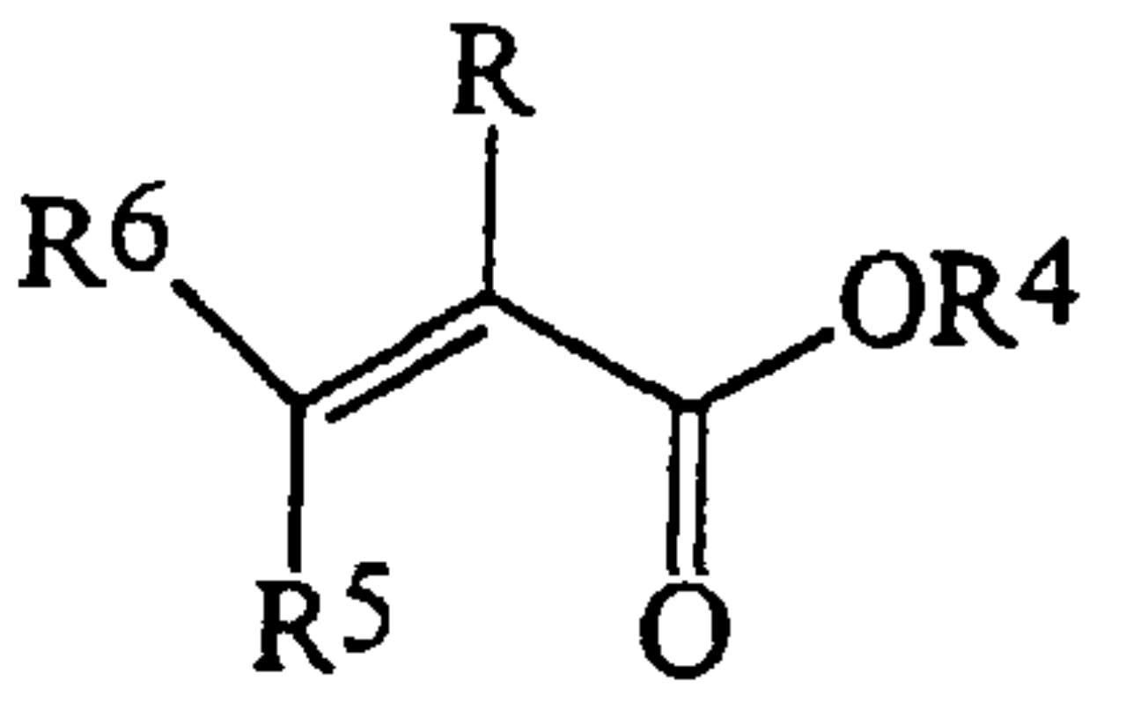
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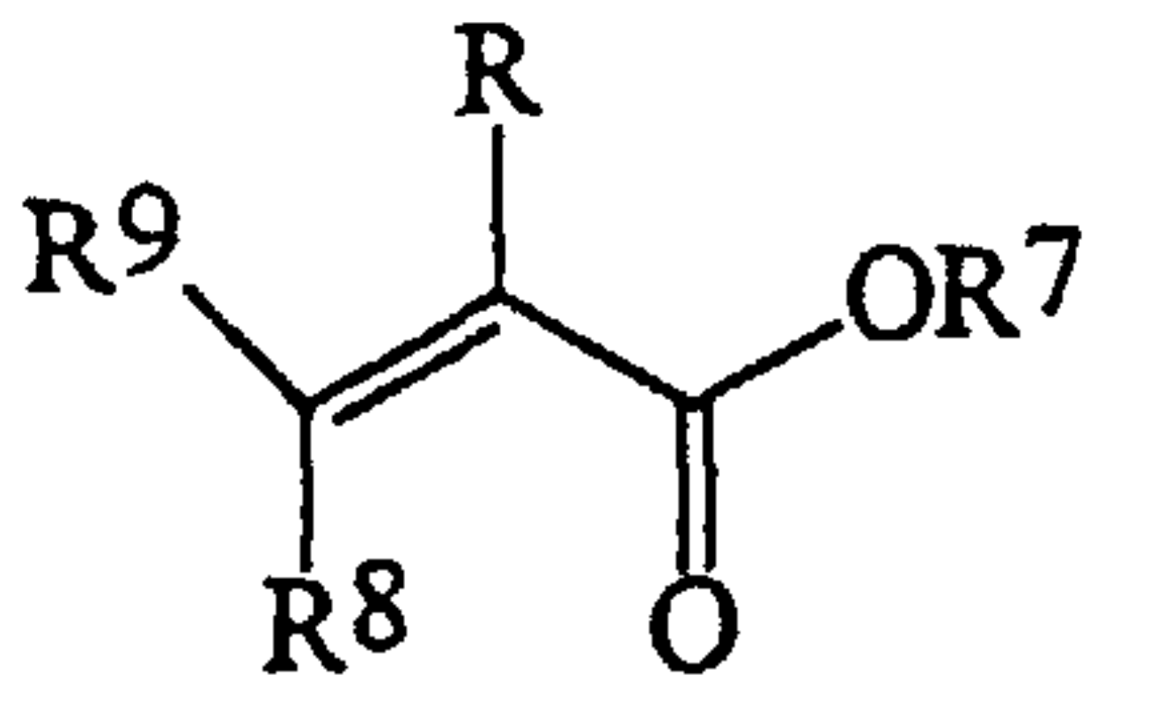
(III)

(57) Abstract: The invention relates to gradient copolymers which can be obtained by polymerizing a mixture of olefinically unsaturated monomers. Said mixture is comprised of: a) 0 to 40 wt. % of one or more ethylenically unsaturated ester compounds of formula (I), wherein R represents hydrogen or methyl, R^1 represents a linear or branched alkyl radical with 1 to 5 carbon atoms, R^2 and R^3 independently represent hydrogen or a group of formula -COOR', wherein R' represents hydrogen or an alkyl group with 1 to 5 carbon atoms, of; b) 10 to 98 wt. % of one or more ethylenically unsaturated ester compounds of formula (II), wherein R represents hydrogen or methyl, R^4 represents a linear or branched alkyl radical with 6 to 15 carbon atoms, R^5 and R^6 independently represent hydrogen or a group of formula -COOR'', wherein R'' represents hydrogen or an alkyl group with 6 to 15 carbon atoms, of; c) 0 to 80 wt. % of one or more ethylenically unsaturated ester compounds of formula (III), wherein R represents hydrogen or methyl, R^7 represents a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9 independently represent hydrogen or a group of formula -COOR''', wherein R''' represents hydrogen or an alkyl group with 16 to 30 carbon atoms, and of; d) 0 to 50 wt. % of comonomers, whereby the mixture of the ethylenically unsaturated monomers is modified during chain growth in order to obtain copolymers, which have a gradient. The novel copolymers are used as setting point improvers.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft Gradientencopolymere, die dadurch erhältlich sind, dass man eine Mischung von olefinisch ungesättigten Monomeren polymerisiert, die aus a) 0 bis 40 Gew.-% einer oder mehreren ethylenisch ungesättigten Esterverbindungen der Formel (I), worin R Wasserstoff oder Methyl darstellt, R^1 einen linearen oder verzweigten Alkylrest mit 1 bis 5 Kohlenstoffatomen bedeutet, R^2 und R^3 unabhängig Wasserstoff oder eine Gruppe der Formel -COOR' darstellen, worin R' Wasserstoff oder eine Alkylgruppe mit 1 bis 5 Kohlenstoffatomen bedeutet, b) 10 bis 98 Gew.-% einer oder mehreren ethylenisch ungesättigten Esterverbindungen der Formel (II), worin R Wasserstoff oder Methyl darstellt, R^4 einen linearen oder verzweigten Alkylrest mit 6 bis 15 Kohlenstoffatomen bedeutet, R^5 und R^6 unabhängig Wasserstoff oder eine Gruppe der Formel -COOR'' darstellen, worin R'' Wasserstoff oder eine Alkylgruppe mit 6 bis 15 Kohlenstoffatomen bedeutet, c) 0 bis 80 Gew.-% einer oder mehreren ethylenisch ungesättigten Esterverbindungen der Formel (III), worin R Wasserstoff oder Methyl darstellt, R^7 einen linearen oder verzweigten Alkylrest mit 16 bis 30 Kohlenstoffatomen bedeutet, R^8 und R^9

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ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW.

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Veröffentlicht:

— *Mit internationalem Recherchenbericht.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

unabhängig Wasserstoff oder eine Gruppe der Formel -COOR''' darstellen, worin R''' Wasserstoff oder eine Alkylgruppe mit 16 bis 30 Kohlenstoffatomen bedeutet, d) 0 bis 50 Gew.-% Comonomer besteht, wobei man die Mischung der ethylenisch ungesättigten Monomere während des Kettenwachstums verändert, um Copolymere zu erhalten, die einen Gradient aufweisen. Die neuen Copolymere finden als Stockpunktverbesserer Anwendung.

Gradient Copolymers
as well as Methods for their Production and Use

The present invention relates to gradient copolymers, concentrates and lubricant oils that contain these copolymers, methods for the production of these copolymers, as well as their use as agents to lower the pour point.

Lubricant oils, particularly mineral oils that are obtained from petroleum by means of distillation, for example, generally contain long-chain n-alkanes that result in a good viscosity/temperature behavior, on the one hand, but on the other hand precipitate in crystalline form when they cool, and thereby impair or completely prevent the flow of the oils ("solidify"). An improvement in the low-temperature flow properties can be achieved, for example, by removing the paraffin. However, the costs increase significantly if complete removal of paraffin is supposed to be achieved. Therefore a pour point up to a range of approximately –15 °C is achieved by means of partial removal of the paraffin, and can be further improved by adding so-called pour-point depressors or pour-point improvement agents. These agents can effectively lower the pour point in concentrations as low as 0.01 to 1 wt.-%.

The method of effect of these compounds has not been fully clarified as yet. However, it is assumed that paraffin-like compounds are built into the growing paraffin crystal surfaces and thereby prevent further crystallization and, in particular, the formation of extensive crystal lattices.

The effect of improving pour point is known for certain structural elements. For example, polymers with sufficiently long alkyl side chains, in particular, demonstrate the effect of improving the pour point. In this connection, it is assumed that these alkyl groups are built into the growing paraffin crystals, and disrupt the crystal growth (see Ullmann's Enzyklopädie der technischen Chemie [Encyclopedia of Technical Chemistry], 4th edition, Volume 20, Verlag Chemie, 1981, p. 548). Furthermore, it must be expected of pour-point depressors that can be used technically, over and above this, that they possess good thermal, oxidative, and chemical stability, shear strength, etc. In addition, it must be possible to produce the pour-point-improving agents in a cost-effective manner, since they are used in large amounts.

Poly(meth)acrylates with long-chain alkyl radicals are used as pour-point depressors, to a great extent. These compounds are described, for example, in U.S. patent 2,091,627, U.S. patent 2,100,993, U.S. patent 2,114,233, and EP-A—0 236 844. In general, these pour-point depressors are obtained by means of radical polymerization. Accordingly, they can be produced in a cost-effective manner.

EP-A-0 861 859 is cited as the closest state of the art. It was found that different pour-point improving agents demonstrate different performance in different lubricant oils. However, if the composition is varied via the reaction time of polymerization, additives are obtained that demonstrate a high level of effectiveness in many mineral oils. Using this method, mixtures of statistical copolymers are produced, since the composition of the monomer mixture remains constant during the lifetime of the radicals (approximately 1 second).

The low-temperature properties that are obtained, for example, from the pour points according to ASTM D-97, the minirotation viscosimetry test values according to ASTM D-4684, or the Scanning-Brookfield results according to ASTM D-5133, are usable for many applications, but in spite of this, the low-temperature properties are still insufficient to satisfy many requirements.

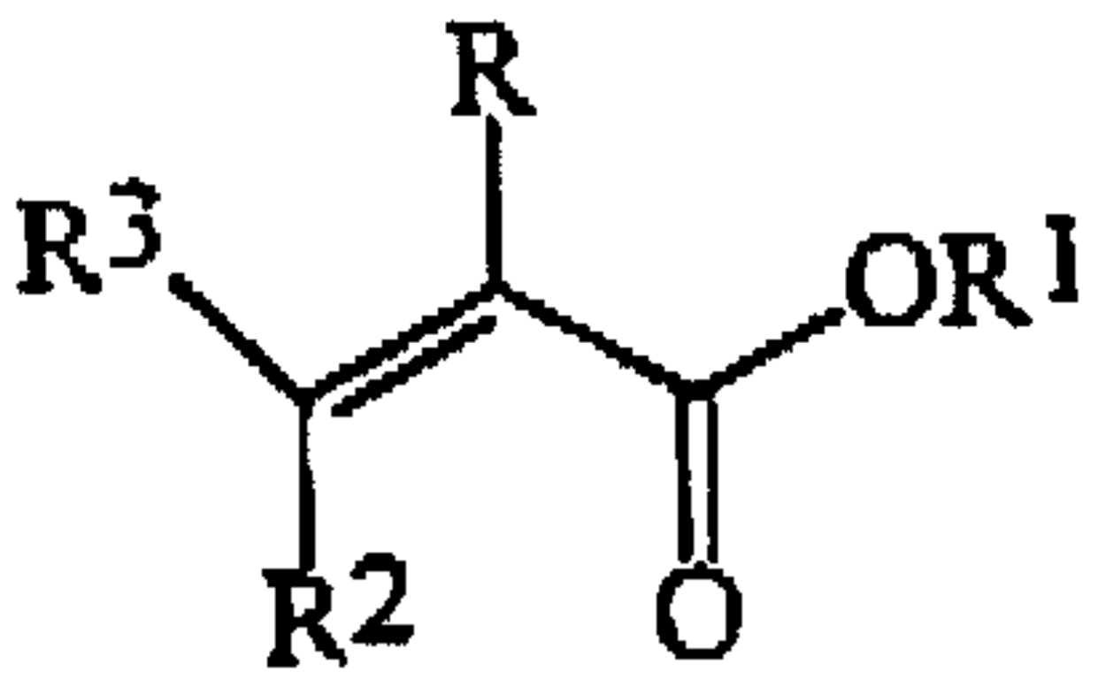
In this connection, it should be taken into consideration that more effective additives could be added in a smaller amount, in order to achieve a desired flow property at low temperatures. With the amounts of lubricant oils and biodiesel fuels that are used, a significant savings potential would result, even if the differences are slight.

In view of the state of the art, it is now the task of the present invention to make additives available, by means of which improved flow properties of lubricant oils and biodiesel fuels can be achieved at low temperatures, in comparison with conventional additives. Furthermore, it was a task of the present invention to make available additives that possess a high level of stability against oxidation and thermal stress, as well as a high shear strength. At the same time, it is supposed to be possible to produce the new additives in a simple and cost-effective manner.

These tasks, as well as others that are not stated explicitly, but can be easily deduced or concluded from the situations discussed in the introduction, are accomplished by gradient copolymers with all the characteristics of Claim 1. Practical modifications of the copolymers according to the invention are protected in the claims that are dependent on Claim 1. With regard to the concentrate as a lubricant oil additive, Claim 6 provides the solution to the underlying task, while Claims 8 and 11 protect lubricant oils and diesel fuels, respectively, that contain copolymers according to the invention. With regard to the method for the production of gradient copolymers and their use, Claims 13 and 14 present a solution for the problem.

Gradient copolymers that demonstrate a high level of effectiveness as pour-point-improving agents or flow-improving agents can be obtained by polymerizing a mixture of olefin-unsaturated monomers that consists of

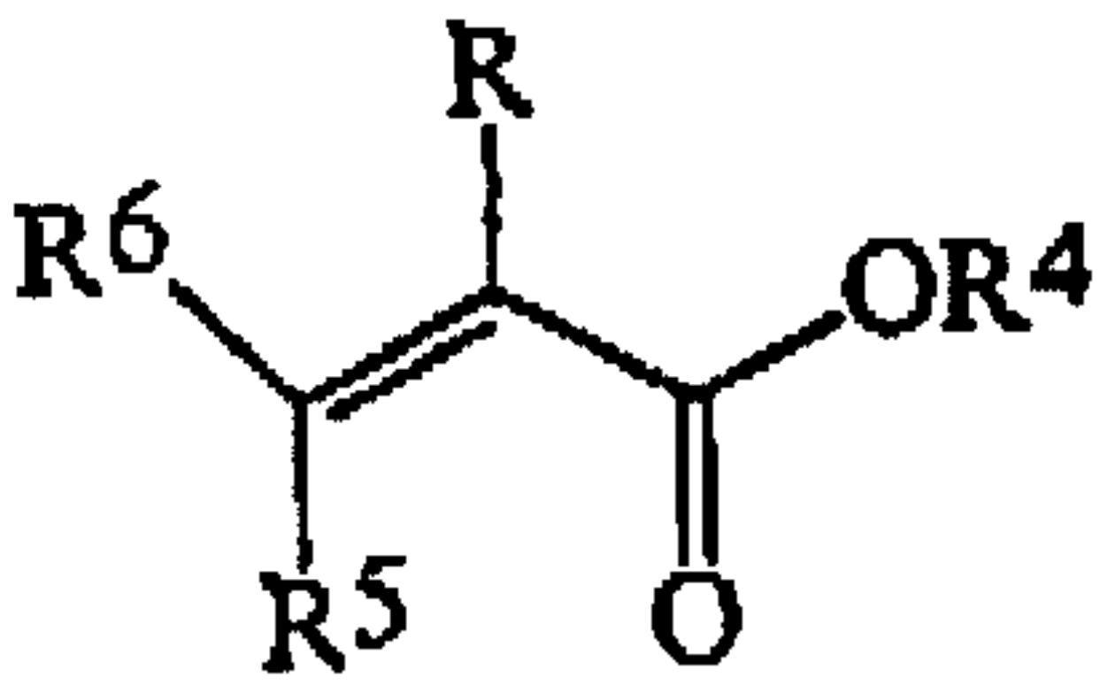
a) 0 to 40 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (I)



(I),

where R stands for hydrogen or methyl, R^1 stands for a linear or branched alkyl radical with 1 to 5 carbon atoms, R^2 and R^3, independently, stand for hydrogen or a group with the formula –COOR', where R' stands for hydrogen or an alkyl group with 1 to 5 carbon atoms,

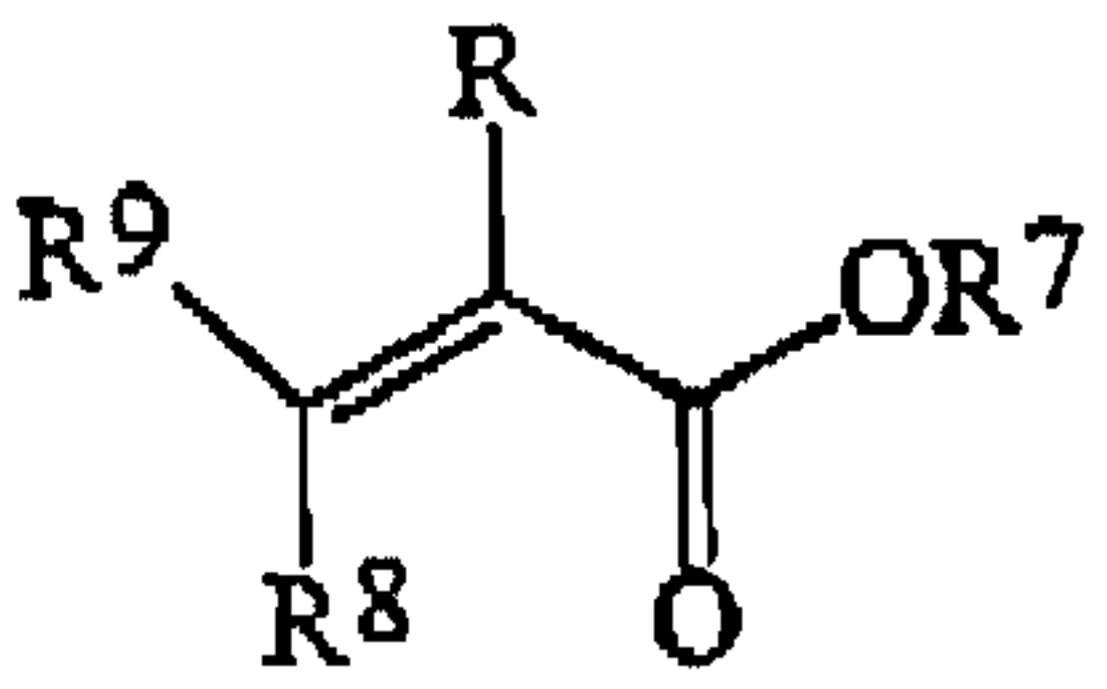
b) 10 to 98 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (II)



(II),

where R stands for hydrogen or methyl, R^4 stands for a linear or branched alkyl radical with 6 to 15 carbon atoms, R^5 and R^6, independently, stand for hydrogen or a group with the formula –COOR'', where R'' stands for hydrogen or an alkyl group with 6 to 15 carbon atoms,

c) 0 to 80 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (III)



(III),

where R stands for hydrogen or methyl, R^7 stands for a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9, independently, stand for hydrogen or a group with the formula –COOR''', where R''' stands for hydrogen or an alkyl group with 16 to 30 carbon atoms,

d) 0 to 50 wt.-% comonomer,

with reference, in each instance, to the total weight of the ethylene-unsaturated monomers, where the mixture of the ethylene-unsaturated monomers is changed during chain growth. The effect of improving the pour point can be determined according to ASTM D 97, for example.

Furthermore, lubricant oils that include the gradient copolymers according to the invention demonstrate excellent minirotation viscosimetry values (MRV), which can be obtained according to ASTM D 4684, and Scanning-Brookfield results, as they are obtained according to ASTM D 5133.

Biodiesel fuels that include a content of gradient copolymers according to the present invention demonstrate extraordinary results in cold-filter-plugging-point measurements according to IP 309 or low-temperature-flow-test results according to ASTM D 4539. If a specific flow property is supposed to be achieved at a pre-determined temperature, the amount of additive can be reduced by means of the present invention.

At the same time, a number of additional advantages can be achieved by means of the gradient copolymers according to the invention. These include, among others:

=> The copolymers of the present invention demonstrate a narrow molecular weight distribution. Because of this, they demonstrate a high level of stability against shear effects.

=> The gradient copolymers according to the invention can be produced in a cost-effective manner.

=> The gradient copolymers demonstrate a high level of oxidation stability and are chemically very resistant.

=> The gradient copolymers demonstrate excellent effectiveness in many different mineral oils or biodiesel fuels.

The term gradient copolymers refers to copolymers that demonstrate a gradient. The term copolymers in and of itself is known and refers to polymers that are obtained by polymerization of two or more different types of monomers.

The term gradient refers to the distribution of the monomer building blocks, also referred to as recurring units, along the main chain of the copolymer. In this connection, the concentration of at least one monomer building block is higher at one end of the chain than at the other end of the polymer chain. If the main chain is divided into 10 equal segments, the concentration of at least one of the recurring units will increase or decrease in at least three consecutive segments. The recurring units result from polymerization from the monomers that are used, in each instance.

An interesting aspect of the present invention is gradient copolymers that are characterized by a linear gradient.

In preferred gradient copolymers with a linear gradient, the concentration of at least one recurring unit increases over at least eight of the ten segments. On the other hand, the increase over all the segments is approximately constant.

Another interesting aspect is gradient copolymers that have a non-linear gradient. These preferred polymers are also characterized in that the concentration of at least one monomer increases over at least eight of the ten segments. However, the increase in the concentration of recurring units is not constant, rather the increase increases over at least three of the nine segments.

Preferred gradient copolymers demonstrate a gradient of at least 5 %, particularly preferably at least 10 %, and very particularly preferably at least 20 %, which relates to the difference in concentration between the first and the last segment.

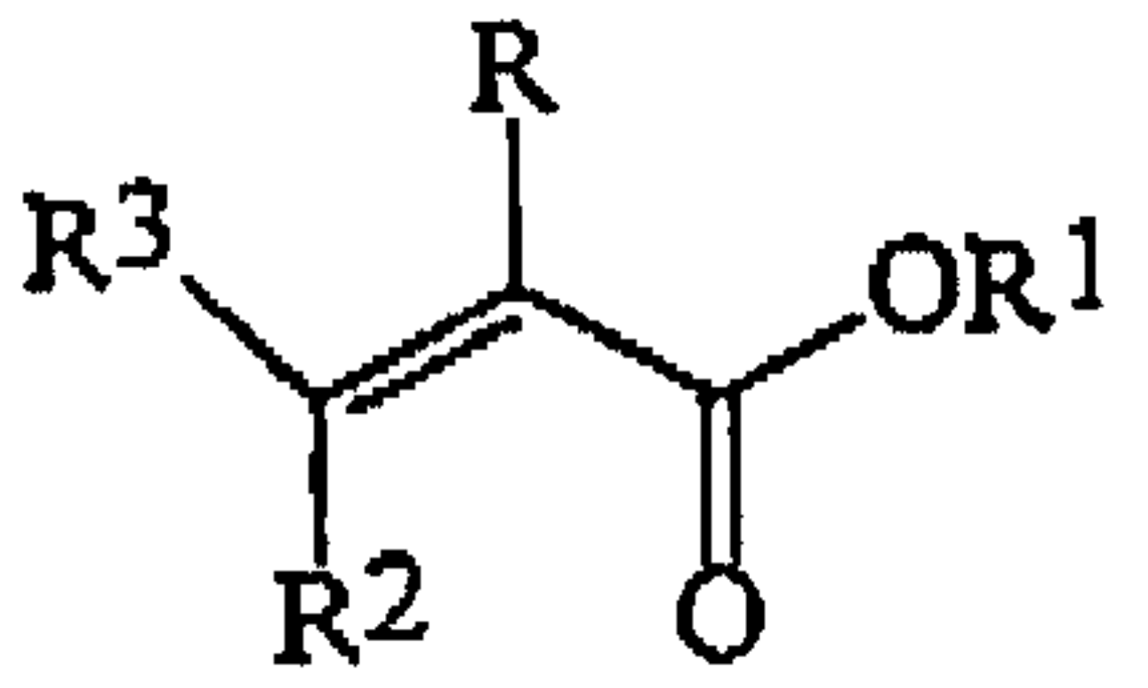
The term “concentration of monomer building blocks” refers to the number of these units that are derived from the monomers used, with reference to the total number of recurring units within a segment. The length of a segment, and therefore the total number, results from the numerical average of the molecular weight M_n, divided by 10, in order to obtain the total number of recurring units of a segment.

Analogously, the term concentration difference means the difference between the concentrations of at least one monomer building block of two segments.

A person skilled in the art is familiar with the polydispersity of polymers. Accordingly, the information with regard to the increase in concentration of at least one recurring unit also refers to a statistical average over all polymer chains of the corresponding segments.

The compositions from which the gradient copolymers according to the invention are obtained particularly contain (meth)acrylates, maleates and/or fumarates that demonstrate different alcohol radicals. The term (meth)acrylates includes methacrylates and acrylates as well as mixtures of them. These monomers are well known. In this connection, the alkyl radical can be linear, cyclic, or branched.

Mixtures from which the gradient copolymers according to the invention can be obtained can contain 0 to 40 wt.-%, particularly 0.5 to 20 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (I)



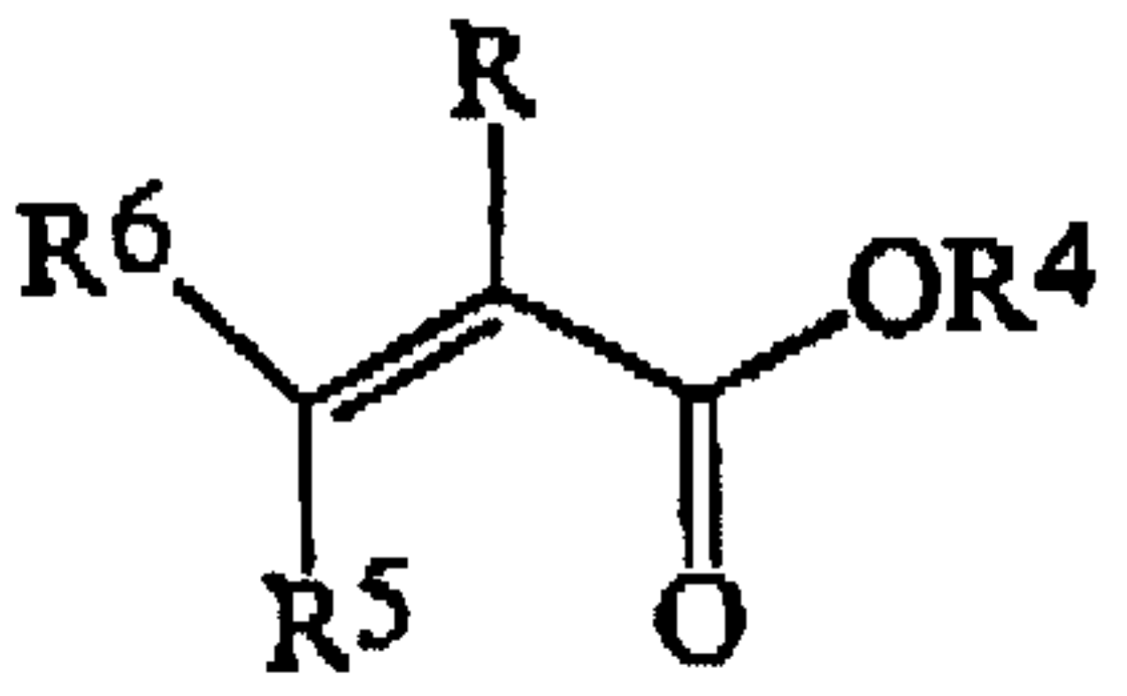
(I),

where R stands for hydrogen or methyl, R^1 stands for a linear or branched alkyl radical with 1 to 5 carbon atoms, R^2 and R^3, independently, stand for hydrogen or a group with the formula –COOR’, where R’ stands for hydrogen or an alkyl group with 1 to 5 carbon atoms.

Examples of Component a) are, among others, (meth)acrylates, fumarates, and maleates that are derived from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, tert.-butyl (meth)acrylate, and pentyl (meth)acrylate;
cycloalkyl (meth)acrylates, such as cyclopentyl (meth)acrylate;

(meth)acrylates that are derived from unsaturated alcohols, such as 2-propinyl (meth)acrylate, allyl (meth)acrylate, and vinyl (meth)acrylate.

As a significant component, the compositions to be polymerized contain 10 to 98 wt.-%, particularly 20 to 95 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (II)

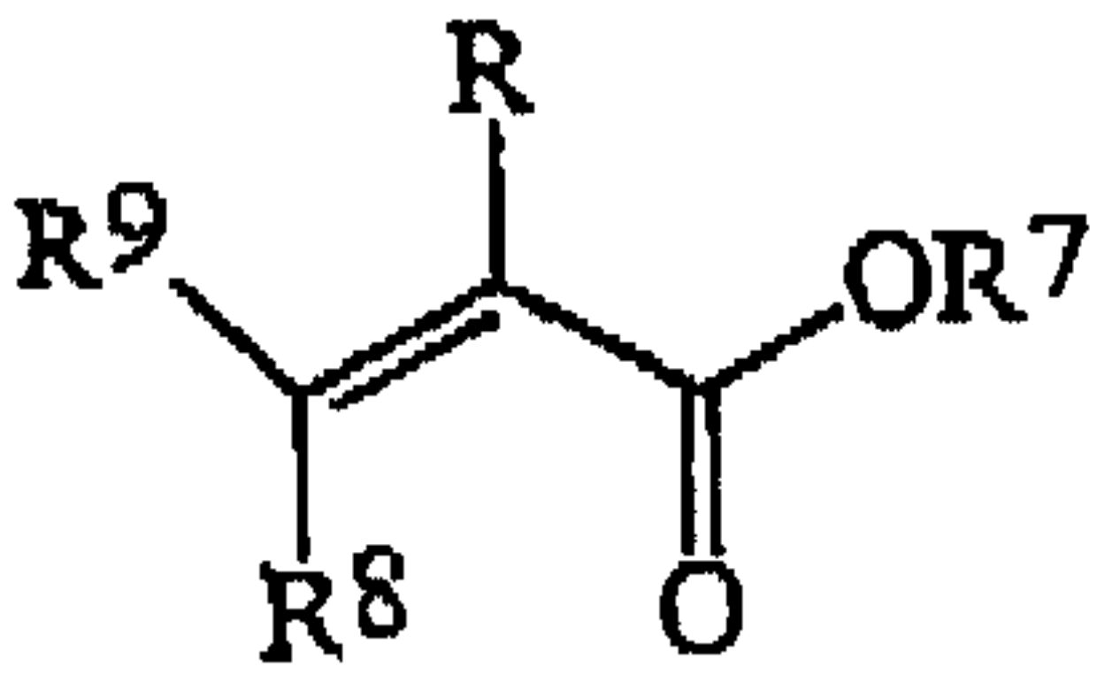


(II),

where R stands for hydrogen or methyl, R^4 stands for a linear or branched alkyl radical with 6 to 15 carbon atoms, R^5 and R^6, independently, stand for hydrogen or a group with the formula –COOR'', where R'' stands for hydrogen or an alkyl group with 6 to 15 carbon atoms.

These include, among others,
(meth)acrylates, fumarates, and maleates that are derived from saturated alcohols, such as hexyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, heptyl (meth)acrylate, 2-tert.-butyl heptyl (meth)acrylate, octyl (meth)acrylate, 3-iso-propyl heptyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methyl undecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyl dodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyl tridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate;
(meth)acrylates that are derived from unsaturated alcohols, such as oleyl (meth)acrylate, for example;
cycloalkyl (meth)acrylates, such as
3-vinyl cyclohexyl (meth)acrylate,
cyclohexyl (meth)acrylate, bornyl (meth)acrylate; as well as the corresponding fumarates and maleates.

Furthermore, the monomer mixtures to be used according to the invention can contain 0 to 80 wt.-%, preferably 0.5 to 60 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (III)



(III),

where R stands for hydrogen or methyl, R^7 stands for a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9, independently, stand for hydrogen or a group with the formula –COOR''', where R''' stands for hydrogen or an alkyl group with 16 to 30 carbon atoms.

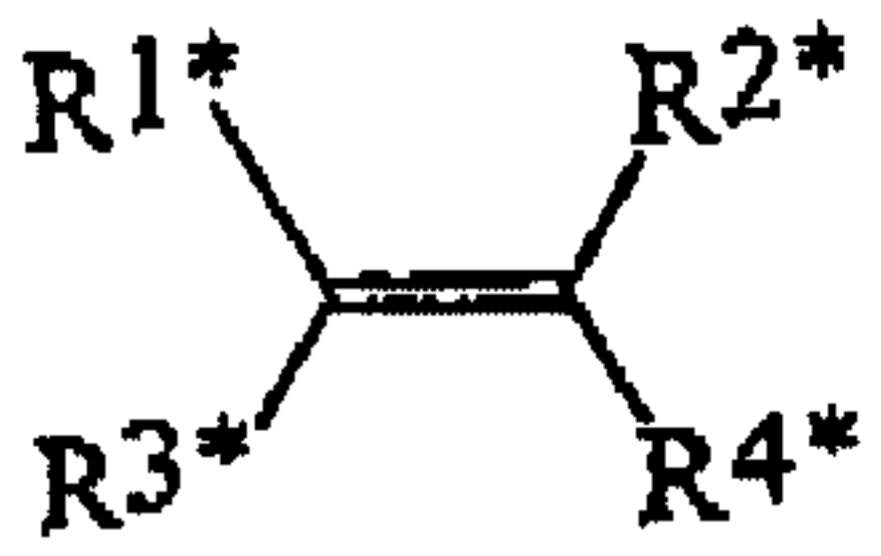
Examples of Component c) are, among others,
(meth)acrylates that are derived from saturated alcohols, such as hexadecyl (meth)acrylate,
2-methyl hexadecyl (meth)acrylate,
heptadecyl (meth)acrylate,
5-iso-propyl heptadecyl (meth)acrylate,
4-tert.-butyl octadecyl (meth)acrylate,
5-ethyl octadecyl (meth)acrylate,
3-iso-propyl octadecyl (meth)acrylate,
octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyl eicosyl (meth)acrylate, stearyl eicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyl tetratriacontyl (meth)acrylate;
cycloalkyl (meth)acrylates, such as 2,4,5-tri-t-butyl-3-vinyl cyclohexyl (meth)acrylate, 2,3,4,5-tetra-t-butyl cyclohexyl(meth)acrylate;
oxiranyl (meth)acrylates, such as
10,11-epoxy hexadecyl methacrylate; as well as the corresponding fumarates and maleates.

The ester compounds with a long-chain alcohol radical, particularly Components (b) and (c), can be obtained, for example, by reaction of (meth)acrylates, fumarates, maleates and/or the corresponding acids with long-chain fatty alcohols, where in general, a mixture of esters is formed, such as (meth)acrylates with different long-chain alcohol radicals, for example. These fatty alcohols include, among others, Oxo Alcohol® 7911, Oxo Alcohol® 7900, and Oxo Alcohol® 1100 from Monsanto; Alphanol® 79 from ICI; Nafol® 1620, Alfol® 610, and Alfol® 810 from Condea; Epal® 610 and Epal® 810 from Ethyl Corporation; Linevol® 79, Linevol® 911, and Dobanol® 25L from Shell AG; Lial 125 from Augusta® Milan; Dehydad® and Lorol® from Henkel KgaA, as well as Linopol® 7 – 11 and Acropol® 91 from Ugine Kuhlmann.

Among the ethylene-unsaturated ester compounds, the (meth)acrylates are particularly preferred as compared with the maleates and fumarates, i.e. in especially preferred embodiments, R^2, R^3, R^5, R^6, R^8, and R^9 in Formulas (I), (II), and (III) represent hydrogen.

The Component d) particularly comprises ethylene-unsaturated monomers that can be copolymerized with the ethylene-unsaturated ester compounds with the Formulas (I), (II), and (III).

However, for polymerization according to the present invention, comonomers that correspond to the following formula are particularly suited:



where R^{1*} and R^{2*}, independently, are selected from the group consisting of hydrogen, halogens, CN, linear or branched alkyl groups with 1 to 20, preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms, which can be substituted with 1 to (2n+1) halogen atoms, where n is the number of carbon atoms in the alkyl group (for example CF_3), α, β unsaturated linear or branched alkenyl or alkynyl groups with 2 to 10, preferably from 2 to 6, and particularly preferably from 2 to 4 carbon atoms, which can be substituted with 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms in the alkyl group, for example CH_2=CCl-, cycloalkyl groups with 3 to 8 carbon atoms, which can be substituted with 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms in the cycloalkyl group; $C(=Y^*)R^{5*}$, $C(=Y^*)NR^{6*}R^{7*}$, $Y^*C(=Y^*)R^{5*}$, SOR^{5*}, SO_2R^{5*}, OSO_2R^{5*}, $NR^{8*}SO_2R^{5*}$, $PR^{5*}{}_2$, $P(=Y^*)R^{5*}{}_2$, $Y^*PR^{5*}{}_2$, $Y^*P(=Y^*)R^{5*}{}_2$, $NR^{8*}{}_2$, which can be quaternized with an additional R^{8*}, aryl or heterocyclyl group, where Y* can be NR^{8*}, S or O, preferably O; R^{5*} is an alkyl group with 1 to 20 carbon atoms, an alkyl thio with 1 to 20 carbon atoms, OR^{15} (R^{15} is hydrogen or an alkali metal) is alkoxy from 1 to 20 carbon atoms, aryloxy, or heterocyclyloxy; R^{6*} and R^{7*}, independently, are hydrogen or an alkyl group with 1 to 20 carbon atoms, or R^{6*} and R^{7*} together can form an alkylene group with 2 to 7, preferably 2 to 5 carbon atoms, where they form a ring with 3 to 8 links, preferably 3 to 6 links, and R^{8*} is hydrogen, linear or branched alkyl or aryl groups with 1 to 20 carbon atoms;

$R3^*$ and $R4^*$ are independently selected from the group consisting of hydrogen, halogen (preferably fluorine or chlorine), alkyl groups with 1 to 6 carbon atoms and $COOR^{9*}$, where R^{9*} is hydrogen, an alkali metal, or an alkyl group with 1 to 40 carbon atoms, or R^{1*} and R^{3*} together can form a group with the formula $(CH_2)_n$, which can be substituted with 1 to 2n' halogen atoms or C_1 to C_4 alkyl groups, or the formula C(=O)-Y*-C(=O), where n' is from 2 to 6, preferably 3 or 4, and Y* is as defined above; and where at least 2 of the radicals R^{1*}, R^{2*}, R^{3*}, and R^{4*} are hydrogen or halogen.

These include, among others,
hydroxyl alkyl (meth)acrylates, such as
3-hydroxypropyl methacrylate,
3,4-dihydroxybutyl methacrylate,
2-hydroxyethyl methacrylate,
2-hydroxypropyl methacrylate,
2,5-dimethyl-1,6-hexane diol (meth)acrylate,
1,10—decane diol (meth)acrylate;

aminoalkyl (meth)acrylates, such as
N-(3-dimethylaminopropyl) methacrylamide,
3-diethylaminopentyl methacrylate,
3-dibutylaminohexadecyl (meth)acrylate;

nitriles of (meth)acrylic acid and other methacrylates that contain nitrogen, such as
N-(methacryloyloxyethyl) diisobutyl ketimine,
N-(methacryloyloxyethyl) dihexadecyl ketimine,
methacryloylamidoacetonitrile,
2-methacryloyloxyethyl methyl cyanamide,
cyanomethyl methacrylate;

aryl (meth)acrylates, such as benzyl methacrylate or phenyl methacrylate, where the aryl radicals can be unsubstituted or substituted up to four times, in each instance;

methacrylates that contain carbonyl, such as
2-carboxyethyl methacrylate,
carboxymethyl methacrylate,
oxazolidinyl ethyl methacrylate,
N-(methacryloyloxy) formamide,
acetonyl methacrylate,
N-methacryloyl morpholine,
N-methacryloyl-2-pyrrolidinone,
N-(2-methacryloyloxyethyl)-2-pyrrolidinone,
N-(3-methacryloyloxypropyl)-2-pyrrolidinone,
N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone,
N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone;

glycol dimethacrylates, such as 1,4-butane diol methacrylate,
2-butoxyethyl methacrylate,

2-ethoxyethoxymethyl methacrylate,
2-ethoxyethyl methacrylate;

methacrylates of ether alcohols, such as
tetrahydrofurfuryl methacrylate,
vinyloxyethoxyethyl methacrylate,
methoxyethoxyethyl methacrylate,
1-butoxypropyl methacrylate,
1-methyl-(2-vinyloxy) ethyl methacrylate,
cyclohexyloxymethyl methacrylate,
methoxymethoxyethyl methacrylate,
benzyloxymethyl methacrylate,
furfuryl methacrylate,
2-butoxyethyl methacrylate,
2-ethoxyethoxymethyl methacrylate,
2-ethoxyethyl methacrylate,
allyloxymethyl methacrylate,
1-ethoxybutyl methacrylate,
methoxymethyl methacrylate,
1-ethoxyethyl methacrylate,
ethoxymethyl methacrylate;

methacrylates of halogenated alcohols, such as
2,3-dibromopropyl methacrylate,
4-bromophenyl methacrylate,
1,3-dichloro-2-propyl methacrylate,
2-bromoethyl methacrylate,
2-iodoethyl methacrylate,
chloromethyl methacrylate;

oxiranyl methacrylates, such as

2,3-epoxybutyl methacrylate,
3,4-epoxybutyl methacrylate,
10,11-epoxyundecyl methacrylate,
2,3-epoxycyclohexyl methacrylate,
glycidyl methacrylate;

methacrylates containing phosphorus, boron and/or silicon, such as
2-(dimethyl phosphato)propyl methacrylate,
2-(ethylene phosphito)propyl methacrylate,
dimethyl phosphinomethyl methacrylate,
dimethyl phosphonoethyl methacrylate,
diethyl methacryloyl phosphonate,
dipropyl methacryloyl phosphate,
2-(dibutyl phosphono)ethyl methacrylate,
2,3-butylene methacryloyl ethyl borate,
methyl diethoxymethacryloylethoxy silane,
diethyl phosphatoethyl methacrylate;

methacrylates containing sulfur, such as
ethyl sulfinyl ethyl methacrylate,
4-thiocyanatobutyl methacrylate,
ethyl sulfonyl ethyl methacrylate,
thiocyanatomethyl methacrylate,
methyl sulfinyl methyl methacrylate,
bis(methacryloyloxyethyl) sulfide;

trimethacrylates, such as
trimethyloyl propane trimethacrylate;

vinyl halogenides, such as, for example, vinyl chloride, vinyl fluoride, vinylidene chloride, and vinylidene fluoride;

heterocyclic (meth)acrylates, such as
2-(1-imidazolyl) ethyl (meth)acrylate,
2-(4-morpholinyl) ethyl (meth)acrylate, and
1-(2-methacryloyloxyethyl)-2-pyrrolidone;

vinyl esters, such as vinyl acetate;

styrene, substituted styrenes with an alkyl substituent in the side chain, such as, for example, α-methyl styrene and α-ethyl styrene, substituted styrenes with an alkyl substituent on the ring, such as vinyl toluene and p-methyl styrene, halogenated styrenes, such as, for example, monochlorostyrenes, dichlorostyrenes, tribromostyrenes, and tetrabromostyrenes;

heterocyclic vinyl compounds, such as 2-vinyl pyridine, 3-vinyl pyridine, 2-methyl-5-vinyl pyridine, 3-ethyl-4-vinyl pyridine, 2,3-dimethyl-5-vinyl pyridine, vinyl pyrimidine, vinyl piperidine, 9-vinyl carbazol, 3-vinyl carbazol, 4-vinyl carbazol, 1-vinyl imidazol, 2-methyl-1-vinyl imidazol, N-vinyl pyrrolidone, 2-vinyl pyrrolidone, N-vinyl pyrrolidine, 3-vinyl pyrrolidine, N-vinyl caprolactam, N-vinyl butyrolactam, vinyl oxolan, vinyl furan, vinyl thiophen, vinyl thiolan, vinyl thiazols, and hydrogenated vinyl thiazols, vinyl oxazols, and hydrogenated vinyl oxazols;

vinyl and isoprenyl ethers;

maleic acid and maleic acid derivatives, such as, for example, monoesters and diesters of maleic acid, maleic acid anhydride, methyl maleic acid anhydride, maleinimide, methyl maleinimide;

fumaric acid and fumaric acid derivatives, such as, for example, monoesters and diesters of fumaric acid;

dienes such as divinyl benzene, for example.

Very particularly preferred mixtures contain methyl methacrylate, butyl methacrylate, lauryl methacrylate, stearyl methacrylate and/or styrene.

These components can be used individually or as mixtures. However, it is a prerequisite that at least two different monomers are polymerized.

Gradient copolymers can be easily characterized using ATRP methods, since these have a living nature. Thus, gradient copolymers can be obtained by continuous variation of the monomer mixture that is present during the chain growth of the individual polymers.

This can be achieved, for example, in that monomers are presented and a different monomer mixture is continuously added to this mixture. In this connection, the monomers that vary over the individual chains are preferably added to the reaction mixture via different feed lines. Continuously means that the duration of the addition is large in relation to the reaction time, in other words the chain growth. This can vary within wide ranges. Without any restriction being intended to result from this, the ratio of the addition time to the total reaction time is greater than 1:10, preferably greater than 1:5, particularly preferably greater than 1:3, and very particularly preferably grater than 1:2.

The aforementioned monomers are polymerized using initiators that have a transferable atom group. In general, these initiators can be described with the formula $Y\text{-}(X)_m$, where Y represents the core molecule, which is assumed to form radicals, X represents a transferable atom or a transferable atom group, and m represents a whole number in the range of 1 to 10, depending on the functionality of the group Y. If $m > 1$, the different transferable atom groups X can have a different meaning. If the functionality of the initiator is > 2, then star-shaped polymers are obtained. Preferred transferable atoms or atom groups are halogens, such as Cl, Br and/or I, for example.

As previously mentioned, it is assumed that the group Y forms radicals that serve as starting molecules, where this radical attaches to the ethylene-unsaturated monomers. Therefore the group Y preferably has substituents that can stabilize radicals. These substituents include, among others, -CN, -COR, and $-CO_2R$, where R represents an alkyl or aryl radical, in each instance, aryl and/or heteroaryl groups.

Alkyl radicals are saturated or unsaturated, branched or linear carbon radicals with 1 to 40 carbon atoms, such as, for example, methyl, ethyl, propyl, butyl, pentyl, 2-methyl butyl, pentenyl, cyclohexyl, heptyl, 2-methyl heptenyl, 3-methyl heptyl, octyl, nonyl, 3-ethyl nonyl, decyl, undecyl, 4-propenyl undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, cetyl eicosyl, docosyl and/or eicosyl tetratriacontyl.

Aryl radicals are cyclic, aromatic radicals that have 6 to 14 carbon atoms in the aromatic ring. These radicals can be substituted. Substituents are, for example, linear and branched alkyl groups with 1 to 6 carbon atoms, such as, for example, methyl, ethyl, propyl, butyl, pentyl, 2-methyl butyl or hexyl; cycloalkyl groups, such as, for example, cyclopentyl or cyclohexyl; aromatic groups, such as phenyl or naphthyl; amino groups, ether groups, ester groups, as well as halogenides.

The aromatic radicals include, for example, phenyl, xylyl, toluyl, naphthyl or biphenyl.

The term “heteroaryl” refers to a heteroaromatic ring system in which at least one CH group is replaced by N, or two adjacent CH groups are replaced by S, O or NH, such as a radical of thiophen, furan, pyrrol, thiazol, oxazol, pyridine, pyrimidine, and benzo[a]furan, which can also contain the aforementioned substituents.

An initiator that can be used according to the invention can be any compound that has one or more atoms or atom groups that can be radically transferred under the polymerization conditions.

Suitable initiators include those with the formulas:
$R^{11}R^{12}R^{13}C\text{-}X$,
$R^{11}C(=O)\text{-}X$,
$R^{11}R^{12}R^{13}Si\text{-}X$,
$R^{11}R^{12}N\text{-}X$,
$R^{11}N\text{-}X_2$,
$(R^{11})_nP(O)_m\text{-}X_{3-n}$,
$(R^{11}O)_nP(O)_m\text{-}X_{3-n}$, and
$(R^{11})(R^{12}O)P(O)_m\text{-}X$,

where X is selected from the group consisting of Cl, Br, I, OR^{10} [where R^{10} represents an alkyl group with 1 to 20 carbon atoms, where each hydrogen atom, independently, can be replaced by a halogenide, preferably fluoride or chloride, alkenyl from 2 to 20 carbon atoms, preferably vinyl, alkynyl from 2 to 10 carbon atoms, preferably acetylenyl, phenyl, which can be substituted with 1 to 5 halogen atoms or alkyl groups with 1 to 4 carbon atoms, or aralkyl (aryl-substituted alkyl, in which the aryl group represents phenyl or substituted phenyl, and the alkyl group represents an alkyl with 1 to 6 carbon atoms, such as benzyl, for example)]; SR^{14}, SeR^{14}, $OC(=O)R^{14}$, $OP(=O)R^{14}$, $OP(=O)(OR^{14})_2$, $OP(=O)OR^{14}$, $O\text{-}N(R^{14})_2$, $S\text{-}C(=S)N(R^{14})_2$, CN, NC, SCN, CNS, OCN, CNO, and N_3, where R^{14} stands for an aryl group or a linear or branched alkyl group with 1 to 20, preferably 1 to 10 carbon atoms, where two R^{14} groups, if they are present, can together form a heterocyclic ring with 5, 6, or 7 links; and R^{11}, R^{12}, and R^{13}, independently, are selected from the group consisting of hydrogen, halogens, alkyl groups with 1 to 20, preferably 1 to 10, and particularly preferably 1 to 6 carbon atoms, cycloalkyl groups with 3 to 8 carbon atoms, $R^{8*}{}_3Si$, $C(=Y^*)R^{5*}$, $C(=Y^*)NR^{6*}R^{7*}$, where Y^*, R^{5*}, R^{6*}, and R^{7*} are as defined above, COCl, OH, (preferably, one of the radicals R^{11}, R^{12}, and R^{13} is OH), CN, alkenyl or alkynyl groups with 2 to 20 carbon atoms, preferably 2 to 6 carbon atoms, and particularly preferably allyl or vinyl, oxiranyl, glycidyl, alkylene or alkenylene groups with 2 to 6 carbon atoms, which are substituted with oxiranyl or glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl (aryl-substituted alkenyl, where aryl is as defined above and alkenyl is vinyl that is substituted with one or two C_1 to C_6 alkyl groups and/or halogen atoms, preferably with chlorine), alkyl groups with 1 to 6 carbon

atoms, in which one to all the hydrogen atoms, preferably one, is/are substituted with halogen (preferably fluorine or chlorine, if one or more hydrogen atoms are replaced, and preferably fluorine, chlorine or bromine, if one hydrogen atom is replaced), alkyl groups with 1 to 6 carbon atoms that are substituted with 1 to 3 substituents (preferably 1) selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, $C(=Y^*)R^{5*}$ (where R^{5*} is as defined above), $C(=Y^*)NR^{6*}R^{7*}$ (where R^{6*} and R^{7*} are as defined above), oxiranyl and glycidyl; (preferably, not more than 2 of the radicals R^{11}, R^{12}, and R^{13} are hydrogen, particularly preferably, a maximum of one of the radicals R^{11}, R^{12}, and R^{13} is hydrogen);
m=0 or 1; and m=0, 1 or 2.

The particularly preferred initiators include benzyl halogenides, such as p-chloromethyl styrene, α-dichloroxylene, α,α-dichloroxylene, α,α-dibromoxylene, and hexakis(α-bromomethyl) benzene, benzyl chloride, benzyl bromide, 1-bromo-1-phenyl ethane, and 1-chloro-1-phenyl ethane;
carboxylic acid derivatives that are halogenated in the α position, such as, for example, propyl-2-bromopropionate, methyl-2-chloropropionate, ethyl-2-chloropropionate, methyl-2-bromopropionate, ethyl-2-bromoisobutyrate;
tosyl halogenides, such as p-toluene sulfonyl chloride;
alkyl halogenides, such as tetrachloromethane, tribromo(meth)ane, 1-vinyl ethyl chloride, 1-vinyl ethyl bromide; and
halogen derivatives of phosphoric acid esters, such as dimethyl phosphoric acid chloride.

The initiator is generally used in a concentration in the range of 10^{-4} mol/L to 3 mol/L, preferably in the range of 10^{-3} mol/L to 10^{-1} mol/L, and particularly preferably in the range of $5*10^{-2}$ mol/L to $5*10^{-1}$ mol/L, without any restriction being intended with this. The molecular weight of the polymer results from the ratio of initiator to monomer, if the entire monomer is reacted. Preferably, this ratio lies in the range of 10^{-4} to 1 to 0.5 to 1, particularly preferably in the range of $5*10^{-3}$ to 1 to $5*10^{-2}$ to 1.

Catalysts that include at least one transition metal are used to carry out the polymerization. In this connection, any transition metal compound that can form a redox cycle with the initiator, i.e. with the polymer chain that has a transferable atom group, can be used. In these cycles, the transferable atom group and the catalyst reversibly form a compound, where the oxidation level of the transition metal is raised or lowered. It is assumed that radicals are released or captured, respectively, in this connection, so that the radical concentration remains very low. However, it is also possible that with the addition of the transition metal compound to the transferable atom group, the insertion of ethylene-unsaturated monomers into the Y-X bond or the $Y(M)_z$-X bond is made possible or facilitated, where Y and X have the meanings as indicated above, and M refers to the monomers, while z represents the degree of polymerization.

Preferred transition metals in this connection are Cu, Fe, Cr, Co, Ne, Sm, Mn, Mo, Ag, Zn, Pd, Pt, Re, Rh, Ir, In, Yd and/or Ru, which are used in suitable oxidation levels. These metals can be used individually or as mixtures. It is assumed that these metals catalyze the redox cycles of the polymerization process, where the redox pair Cu^+/Cu^{2+} or Fe^{2+}/Fe^{3+} is active, for example. Accordingly, the metal compounds are added to the reaction mixture as halogenides, such as, for example, chloride or bromide, as alkoxide, hydroxide, oxide, sulfate, phosphate, or hexafluorophosphate, trifluoromethane sulfate. The preferred metallic compounds include Cu_2O, CuBr, CuCl, CuI, CuN_3, CuSCN, CuCN, $CuNO_2$, $CuNo_3$, $CuBF_4$, $Cu(CH_3COO)$, $Cu(CF_3COO)$, $FeBr_2$, $RuBr_2$, $CrCl_2$, and $NiBr_2$.

However, compounds in higher oxidation levels, such as, for example, $CuBr_2$, $CuCl_2$, CuO, $CrCl_3$, Fe_2O_3, and $FeBr_3$, can also be used. In these cases, the reaction can be initiated using conventional radical-forming agents, such as, for example, AIBN. In this connection, the transition metal compounds are first reduced, since they are reacted with the radicals that are formed from the conventional radical-forming agents. This is reverse ATRP, as it was described by Wang and Matyjaszewski in Macromolecules (1995), Vol. 28, p. 7572-7573.

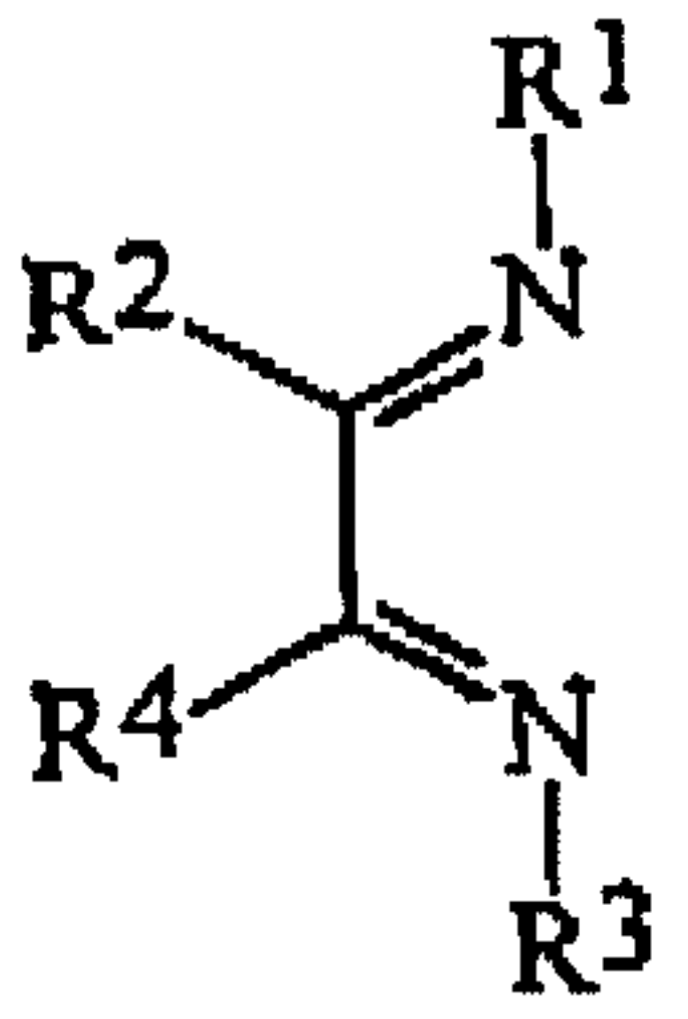
Furthermore, the transition metals can be used for catalysis in the oxidation level zero, particularly in a mixture with the aforementioned compounds, as is described, for example, in WO 98/40415. In these cases, the reaction speed of the reaction can be increased. It is assumed that in this way, the concentration of catalytically active transition metal compound is increased, in that transition metals with a high oxidation level react in proportion with metallic transition metal.

The molar ratio of transition metal to initiator generally lies in the range of 0.0001:1 to 10:1, preferably in the range of 0.001:1 to 5:1, and particularly preferably in the range of 0.01 to 2:1, without any restriction being intended by this.

The polymerization takes place in the presence of ligands that can form a coordination compound with the metallic catalyst(s). These ligands serve, among other things, to increase the solubility of the transition metal compound. Another important function of the ligands is to prevent the formation of stable organometal compounds. This is particularly important, since these stable compounds would not polymerize under the reaction conditions selected. Furthermore, it is assumed that the ligands facilitate the abstraction of the transferable atom group.

These ligands are known and have been described, for example, in WO 97/18247, WO 98/40415. These compounds generally have one or more nitrogen, oxygen, phosphorus and/or sulfur atoms, by way of which the metal atom can be bound. Many of these ligands can generally be described with the formula R^{16}-Z-(R^{18}-Z)$_m$-R^{17}, where R^{16} and R^{17}, independently, stand for H, C_1 to C_{20} alkyl, aryl, heterocyclyl, which can be substituted, if necessary. These substituents include, among other things, alkoxy radicals and alkylamino radicals. R^{16} and R^{17} can, if necessary, form a saturated, unsaturated or heterocyclic ring. Z stands for O, S, NH, NR^{19} or PR^{19}, where R^{19} has the same meaning as R^{16}. R^{18}, independently, stands for a divalent group with 1 to 40 C atoms, preferably 2 to 4 C atoms, which can be linear, branched, or cyclic, such as, for example, a methylene, ethylene, propylene or butylene group. The meaning of alkyl and aryl was explained above. Heterocyclyl radicals are cyclic radicals with 4 to 12 carbon atoms, in which one or more of the CH_2 groups of the ring are replaced by hetero atom groups, such as O, S, NH, and/or NR, where the radical R has the same meaning as R^{16}.

Another group of suitable ligands can be characterized by the formula



(IV),

where R^1, R^2, R^3, and R^4, independently, stand for H, C_1 to C_{20} alkyl, aryl, heterocyclyl and/or heteroaryl radicals, where the radicals R^1 and R^2 together, and R^4 and R^3 together, respectively, can form a saturated or unsaturated ring.

In this connection, preferred ligands are chelate ligands that contain N atoms.

The preferred ligands include, among others, triphenyl phosphane, 2,2-bipyridine, alkyl-2,2-bipyridine, such as 4,4-di-(5-nonyl)-2,2-bipyridine, 4,4-di-(5-heptyl)-2,2-bipyridine, tris(2-aminoethyl)amine (TREN), N,N,N',N',N''-pentamethyl diethylene triamine, 1,1,4,7,10,10-hexamethyl triethylene tetramine and/or tetramethylethylene diamine. Additional preferred ligands are described, for example, in WO 97/47661. The ligands can be used individually or as mixtures.

These ligands can form coordination compounds with the metal compounds in situ, or they can first be produced as coordination compounds and subsequently be added to the reaction mixture.

The ratio of ligand to transition metal is dependent on the viscosity of the ligand and the coordination number of the transition metal. In general, the molar ratio lies in the range of 100:1 to 0.1:1, preferably 6:1 to 0.1:1, and particularly preferably 3:1 to 0.5:1, without any restriction being intended by this.

The monomers, the transition metals, the ligands, and the initiators are selected as a function of the desired polymer solution. It is assumed that a high speed constant of the reaction between the transition metal/ligand complex and the transferable atom group is essential for a narrow molecular weight distribution. If the speed constant of this reaction is too low, the concentration of radicals will become too high, so that the typical truncation reactions that are responsible for a broad molecular weight distribution occur. The exchange rate, for example, is dependent on the transferable atom group, the transition metal, the ligand, and the anion of the transition metal compound. A person skilled in the art will find valuable information concerning the selection of these components in WO 98/40415, for example.

In addition to the ATRP method explained above, the gradient copolymers according to the invention can also be obtained, for example, using RAFT methods ("reversible addition fragmentation chain transfer"). This method is explained in detail in WO 98/04178, for example, and for purposes of disclosure, explicit reference is made to this document.

The polymerization can be carried out under normal pressure, partial vacuum, or higher pressure. The polymerization temperature is also not critical. In general, however, it lies in the range of –20 - 200 °C, preferably 0 – 130 °C, and particularly preferably 60 – 120 °C.

The polymerization can be carried out with or without solvents. In this connection, the term solvent is to be understood in a broad sense.

Preferably, the polymerization is carried out in a non-polar solvent. This includes hydrocarbon solvents, such as, for example, aromatic solvents, such as toluene, benzene, and xylene, saturated hydrocarbons, such as, for example, cyclohexane, heptane, octane, nonane, decane, dodecane, which can also be present in branched form. These solvents can be used individually or as mixtures. Particularly preferred solvents are mineral oils and synthetic oils as well as mixtures of them. Of these, mineral oils are very particularly preferred.

Mineral oils are known and are commercially available. They are generally obtained from petroleum or crude oil, by means of distillation and/or refining, and, if necessary, additional purification and processing steps, where the term mineral oil particularly includes the portions of crude oil or petroleum with a higher boiling point. In general, the boiling point of mineral oil lies above 200 °C, preferably above 300 °C, at 50 mbar. It is also possible to produce them by means of low-temperature distillation of shale oil, coking of hard coal, distillation of brown coal with the exclusion of air, as well as hydrogenation of hard coal or brown coal. To a lesser extent, mineral oils are also produced from raw materials with a vegetable origin (e.g. from jojoba, canola) or animal origin (e.g. neat's foot oil). Accordingly, mineral oils have different proportions of aromatic, cyclic, branched, and linear hydrocarbons, depending on their origin.

In general, a differentiation is made between paraffin-basic, naphthenic, and aromatic components in crude oils or mineral oils, where the term paraffin-basic component stands for iso-alkanes with longer chains or a lot of branching, and the term naphthenic component stands for cycloalkanes. In addition, mineral oils contain different amounts of n-alkanes, iso-alkanes with a lower degree of branching, so-called monomethyl-branched paraffins, and compounds with hetero atoms, particularly O, N and/or S, depending on their origin and processing, and polar properties are ascribed to these. The proportion of n-alkanes in preferred mineral oils is less than 3 wt.-%, the proportion of compounds containing O, N and/or S is less than 6 wt.-%. The proportion of aromatics and monomethyl-branched paraffins is generally in the range of 0 to 30 wt.-%, in each instance. In accordance with an interesting aspect, mineral oil mainly comprises naphthenic and paraffin-basic alkanes, which generally have more than 13, preferably more than 18, and particularly preferably more than 20 carbon atoms. The proportion of these compounds is generally ≥ 60 wt.-%, preferably ≥ 80 wt.-%, without any restriction being intended by this.

An analysis of particularly preferred mineral oils that took place using conventional methods, such as urea separation and liquid chromatography on silica gel, showed the following components, for example, where the percentage information relates to the total weight of the mineral oil being used, in each instance:
n-alkanes with approximately 18 to 31 C atoms:
0.7 – 1.0 %,
slightly branched alkanes with 18 to 31 C atoms:
1.0 – 8.0 %,
aromatics with 14 to 32 C atoms:
0.4 – 10.7 %,
iso-alkanes and cyclo-alkanes with 20 to 32 C atoms:
60.7 – 82.4 %,
polar compounds:
0.1 – 0.8 %,
loss:
6.9 – 19.4 %.

Valuable information with regard to the analysis of mineral oils, as well as a listing of mineral oils that have a different composition can be found, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition on CD-ROM, 1997, key word "lubricants and related products."

Synthetic oils are, among other things, organic esters, such as silicone oils, and synthetic hydrocarbons, particularly polyolefins. They are generally somewhat more expensive than mineral oils, but have advantages with regard to their performance capacity. To make this clear, the 5 API classes of the basic oil types (API: American Petroleum Institute) will be discussed, with these base oils being particularly preferred for use as solvents.

These solvents can be used, among other things, in an amount of 1 to 99 wt.-%, preferably from 5 to 95 wt.-%, particularly preferably from 5 to 60 wt.-%, and very particularly preferably from 10 to 50 wt.-%, with reference to the total weight of the mixture, without any restriction being intended by this.

The polymers produced in this way generally have a molecular weight in the range of 1,000 to 1,000,000 g/mol, preferably in the range of $10*10^3$ to $500*10^3$, and particularly preferably in the range of $20*10^3$ to $300*10^3$ g/mol, without any restriction being intended by this. These values relate to the weight average of the molecular weight of the polydisperse polymers in the composition.

The particular advantage of ATRP in comparison with conventional radical polymerization methods is that polymers with a narrow molecular weight distribution can be produced. Without any restriction being intended by this, the polymers according to the invention demonstrate a polydispersity, which is determined by M_w/M_n, in the range of 1 to 12, preferably 1 to 4.5, particularly preferably 1 to 3, and very particularly preferably 1.05 to 2.

Copolymers produced according to the invention are used, among other things, as additives to lubricant oils and biodiesel fuels, in order to lower the pour point. Therefore, other interesting aspects of the present invention are lubricant oils and biodiesel fuels that contain copolymers according to the invention.

The copolymers according to the invention can be used individually or as a mixture, where the term mixture is to be understood in a broad sense. It includes both mixtures of different copolymers of the present invention and mixtures of copolymers according to the invention with conventional polymers.

Biodiesel fuels are known, and the term refers to natural, particularly renewable oils that are suitable for operating specially adapted diesel engines. These fuels include vegetable oils, such as canola oil, for example.

Examples of lubricant oils are, among other things, motor oils, transmission oils, turbine oils, hydraulic fluids, pump oils, heat transfer oils, insulation oils, cutting oils, and cylinder oils.

In general, these lubricant oils contain a base oil as well as one or more additives, which are well known among persons skilled in the art.

In principle, any base oil that provides a sufficient lubricant film, which does not tear even at high temperatures, is suitable as a base oil. Viscosity can be used to determine this property, for example the viscosity as determined for motor oils in the SAE specifications.

The compounds that are suitable for this purpose include, among other things, natural oils, mineral oils, and synthetic oils, as well as mixtures of these.

Natural oils are animal or vegetable oils, such as, for example, neat's foot oils or jojoba oils. Mineral oils were described in detail above, as solvents. They are particularly advantageous because of their low price. Synthetic oils are, among other things, organic esters, synthetic hydrocarbons, particularly polyolefins, that satisfy the requirements indicated above. They are generally somewhat more expensive than mineral oils, but they have advantages with regard to their performance capacity.

These base oils can also be used as mixtures, and many of them are commercially available.

The copolymers according to the invention can also be used as a component of so-called DI packages (detergent inhibitor) or other concentrates that are added to lubricant oils, which are widely known. These concentrates comprise 15 to 85 wt.-% of one or more copolymers according to the present invention. In addition, the concentrate can also contain organic solvents, particularly a mineral oil and/or a synthetic oil.

Lubricant oils, or the concentrates mentioned above, generally contain additives, in addition to the base oil. These additives include, among other things, viscosity index improving agents, antioxidants, anti-aging agents, corrosion inhibitors, detergents, dispersants, EP additives, anti-foaming agents, friction reducers, pour-point depressors, dyes, fragrances and/or demulsifiers.

The additives result in good flow behavior at low and high temperatures (improving the viscosity index), they suspend solids (detergent/dispersant behavior), neutralize acidic reaction products, and form a protective film on the cylinder surface (EP additive, for "extreme pressure"). A person skilled in the art will find additional valuable information in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition on CD-ROM, 1998 edition.

The amounts in which these additives are used are dependent on the area of use of the lubricant. In general, however, the proportion of base oil is between 25 and 90 wt.-%, preferably 50 to 75 wt.-%. The proportion of copolymers according to the present invention in lubricant oils is preferably in the range of 0.01 to 10 wt.-%, particularly preferably in the range of 0.01 to 2 wt.-%. Biodiesel fuels preferably contain the copolymers according to the present invention in an amount in the range of 0.01 to 10 wt.-%, particularly preferably 0.01 to 2 wt.-%.

In the following, the invention will be explained in greater detail using examples and comparison examples, but without any intent to restrict the invention to these examples.

In the following experiments, the pour points were determined according to ASTM D 97-93, the MRV values were determined according to ATSM 4684-92, and the Scanning-Brookfield result was determined according to ASTM D 5133-90. The gelation index is the maximum of the first mathematical derivation of the viscosity/temperature diagram of the Scanning-Brookfield measurement. With regard to the yield-stress value of the MRV measurement, it should be taken into consideration that measurement values below 35 Pa are indicated with a value of 0, because of the measurement accuracy.

Examples and Comparison Example

The ATRP polymerization experiments were carried out in a round flask equipped with a saber stirrer, heating mushroom, nitrogen atmosphere, intensive cooler, and drip funnel. First, 100 g of the SMA/LMA mixture (SMA: a mixture of long-chain methacrylates that was obtained from the reaction of methyl methacrylate with ®Dehydad from Henkel KgaA; LMA: a mixture of long-chain methacrylates that was obtained from the reaction of methyl methacrylate with ®Lorol from Henkel KgaA) with a weight ratio of 41:59 were presented in a reaction flask, together with 50 g mineral oil from Petro Canada, and made inert by adding dry ice and passing nitrogen over the mixture. Subsequently, the mixture was heated to 95 °C, while stirring. During the heating process, 0.52 g CuBr and 1.26 g PMDETA (pentamethyl diethylene triamine) were added at approximately 70 °C. After the pre-determined temperature of 95 °C had been reached, 0.71 g EbiB (ethyl-2-bromoisobutyrate) were added, causing a heterogeneous mixture to form, since the catalyst had not dissolved completely.

After a reaction time of 15 minutes at 95 °C, the addition of 100 g SMA/LMA mixture with an SMA:LMA weight ratio of 48:52 was started. The addition took place at a constant run-in speed, over a time period of 2 hours. After the addition was complete, stirring continued for another 2 hours at 95 °C.

Subsequently, the mixture was cooled to room temperature, diluted with approximately 400 ml toluene, and filtered over 10 g Al_2O_3, in order to remove contaminants. Afterwards, the toluene that was used was distilled off with a rotation evaporator. This mixture was analyzed by means of GPC, in order to determine the numerical average of the molecular weight (Mn) and the polydispersity Mw/Mn (PDI).

Subsequently, the amount of the polymer obtained in this way, as indicated in Table 1, was mixed with a 15W-40 (SAE) motor oil for passenger cars, consisting of a mixture of a Group I and a Group II mineral oil (weight ratio 1:4). Afterwards, the effectiveness of the additive was tested in accordance with the experiments stated above. The results obtained were also listed in Table 1.

For comparison purposes, a copolymer mixture was produced in accordance with EP-A-0861 859. Here, the same mixtures (41:59 and 48:52 SMA:LMA mixtures) were used. However, it was not gradient copolymers but rather physical mixtures of statistical copolymers that were obtained, since the lifetime of the radicals formed during polymerization is short in relation to the change in the monomer mixture.

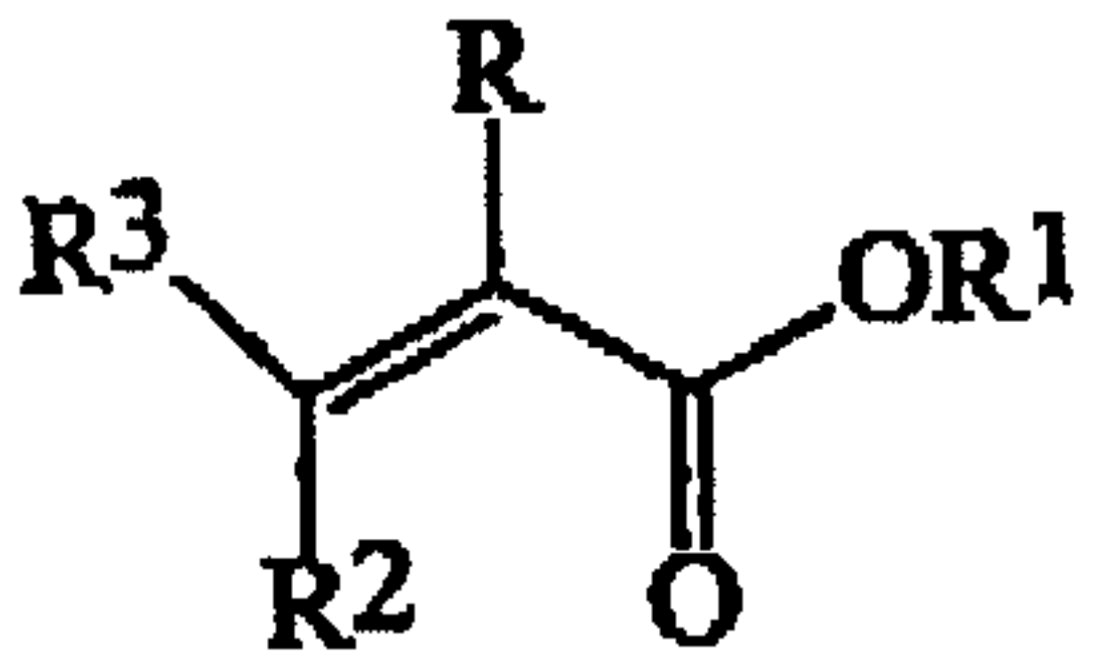
Table 1

	Example 1	Example 2	Comparison
Mn	56,100	56,100	55,800
PDI	1.35	1.35	2.34
Polymer content of the mixture (wt.-%)	0.024	0.036	0.03
Pour point	-42	-45	-39
MRV			
Viscosity (Pa*s)	25.7	25.7	31.3
Yield stress (Pa)	0	0	0
Scanning-Brookfield			
Viscosity at –20 °C (mPa*s)	12,000	39,000	solid
Temperature at 30,000 mPa*s (°C)	-34.5	-28.8	-26.1
Gelation index at °C	5.8 at –13	9.9 at -24	13.8 at –22

AMENDED CLAIMS

1. Gradient copolymers that can be obtained by polymerizing a mixture of olefin-unsaturated monomers that consists of

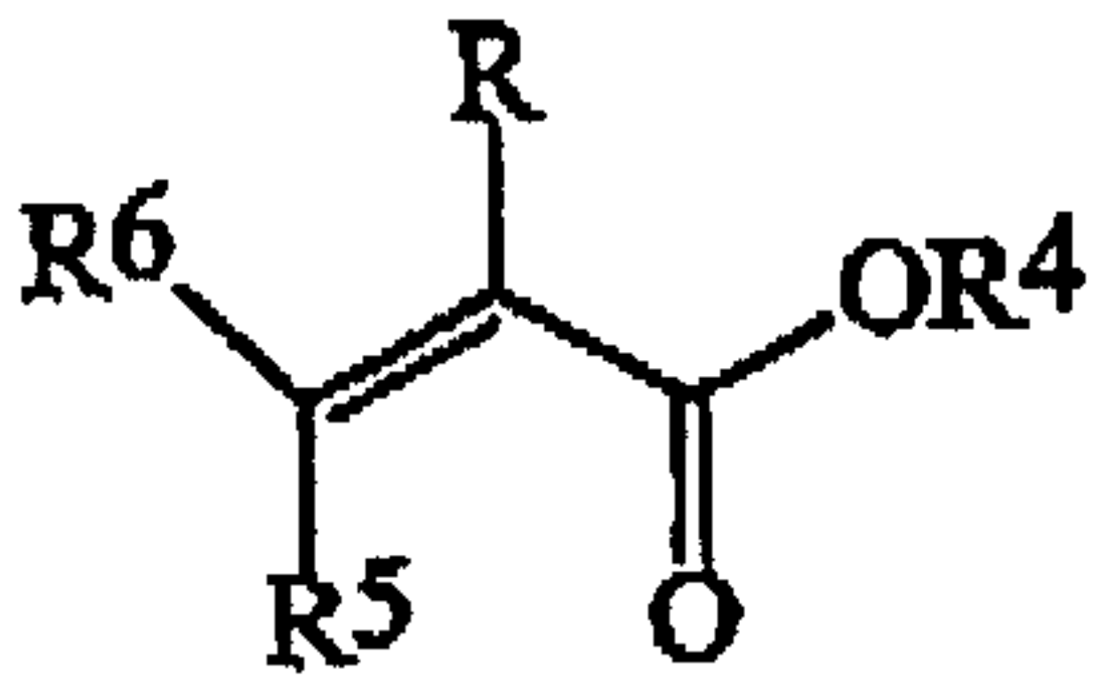
a) 0 to 40 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (I)



(I),

where R stands for hydrogen or methyl, R^1 stands for a linear or branched alkyl radical with 1 to 5 carbon atoms, R^2 and R^3, independently, stand for hydrogen or a group with the formula –COOR', where R' stands for hydrogen or an alkyl group with 1 to 5 carbon atoms,

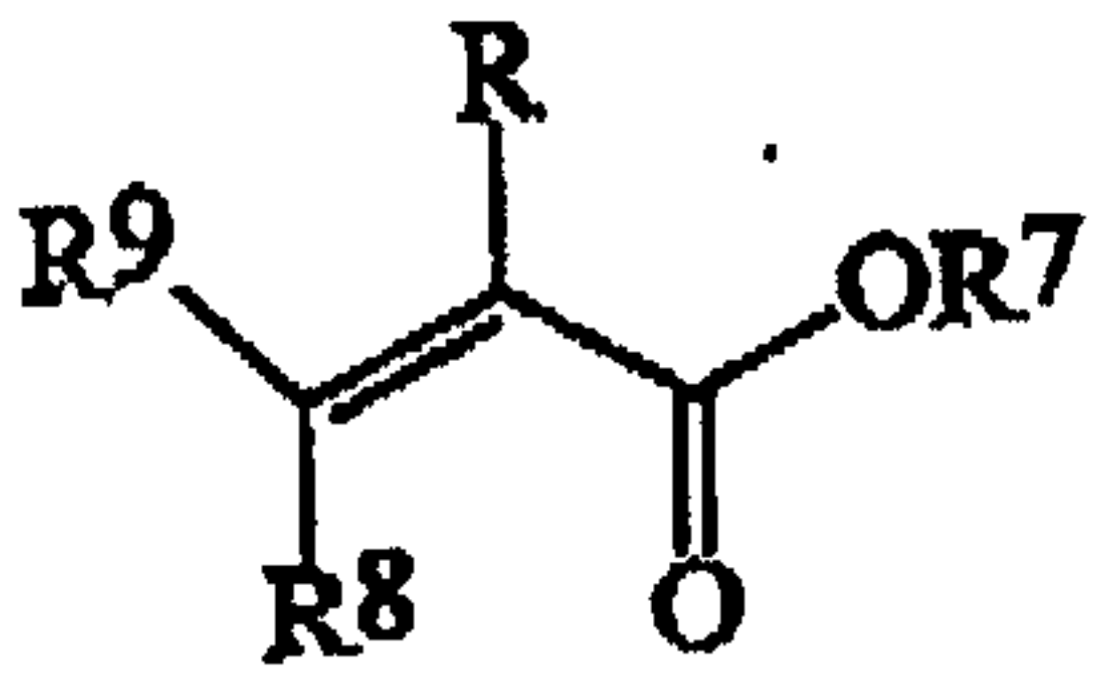
b) 10 to 98 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (II)



(II),

where R stands for hydrogen or methyl, R^4 stands for a linear or branched alkyl radical with 6 to 15 carbon atoms, R^5 and R^6, independently, stand for hydrogen or a group with the formula –COOR'', where R'' stands for hydrogen or an alkyl group with 6 to 15 carbon atoms,

c) 0 to 80 wt.-% of one or more ethylene-unsaturated ester compounds with the Formula (III)

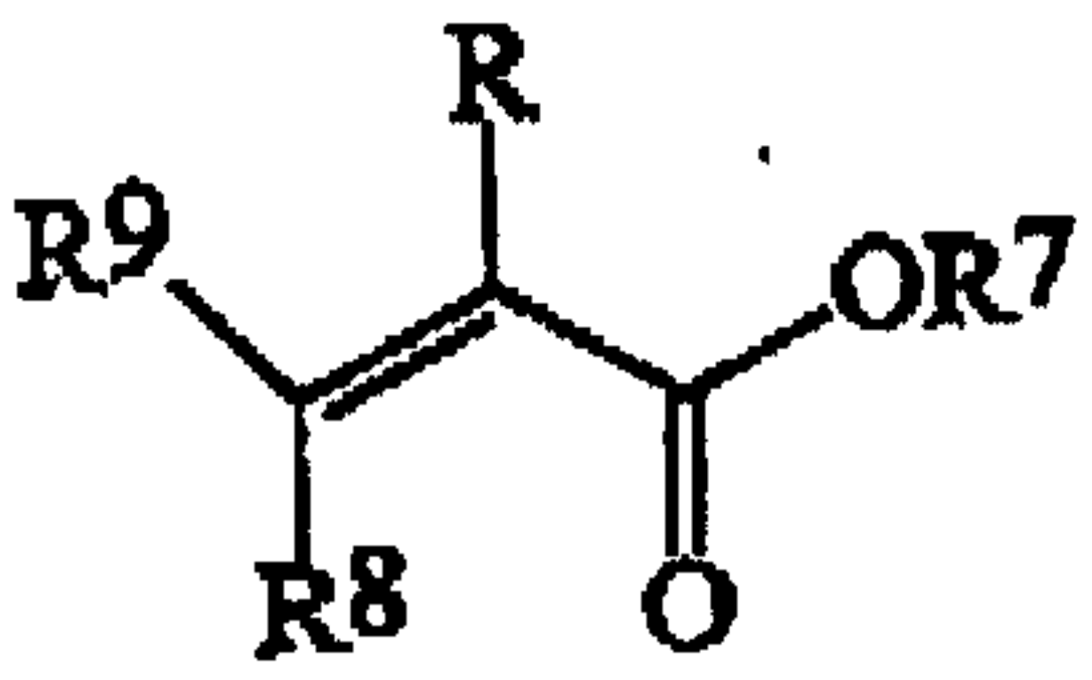


(III),

where R stands for hydrogen or methyl, R^7 stands for a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9, independently, stand for hydrogen or a group with the formula –COOR''', where R''' stands for hydrogen or an alkyl group with 16 to 30 carbon atoms,

d) 0 to 50 wt.-% comonomer,

with reference, in each instance, to the total weight of the ethylene-unsaturated monomers, where the mixture of the ethylene-unsaturated monomers is changed during chain growth, in order to obtain copolymers that demonstrate a gradient, and where at least two different monomers are polymerized.



(III),

where R stands for hydrogen or methyl, R^7 stands for a linear or branched alkyl radical with 16 to 30 carbon atoms, R^8 and R^9, independently, stand for hydrogen or a group with the formula –COOR''', where R''' stands for hydrogen or an alkyl group with 16 to 30 carbon atoms,

d) 0 to 50 wt.-% comonomer,

with reference, in each instance, to the total weight of the ethylene-unsaturated monomers, where the mixture of the ethylene-unsaturated monomers is changed during chain growth, in order to obtain copolymers that demonstrate a gradient.

2. Gradient copolymers according to Claim 1, characterized in that the gradient of the copolymer is more than 5 %.

3. Gradient copolymers according to Claim 1 or 2, characterized in that the copolymer has a linear gradient.

4. Gradient copolymers according to one or more of the preceding claims, characterized in that the weight average of the molar mass of the copolymer lies in the range of 10,000 – 500,000 g/mol.

5. Gradient copolymers according to one or more of the preceding claims, characterized in that the polydispersity (M_w/M_n) lies in the range of 1 to 12, particularly of 1.05 to 2.

6. Concentrate as a lubricant oil additive, characterized in that the concentrate contains 15 to 85 wt.-% of one or more gradient copolymers according to one or more of Claims 1 to 5.

7. Concentrate according to Claim 6, characterized in that the concentrate additionally contains organic solvents, particularly a mineral oil and/or a synthetic oil.

8. Lubricant oil containing gradient copolymers according to one or more of Claims 1 to 5.

9. Lubricant oil according to Claim 8, characterized in that the gradient copolymer according to one of Claims 1 to 5 is present in an amount in the range of 0.01 to 10 wt.-%, particularly 0.01 to 2 wt.-%.

10. Concentrate according to Claim 6 or lubricant oil according to Claim 8, characterized in that in addition, it contains viscosity index improving agents, antioxidants, corrosion inhibitors, detergents, dispersants, EP additives, anti-foaming agents, friction reducers and/or demulsifiers.

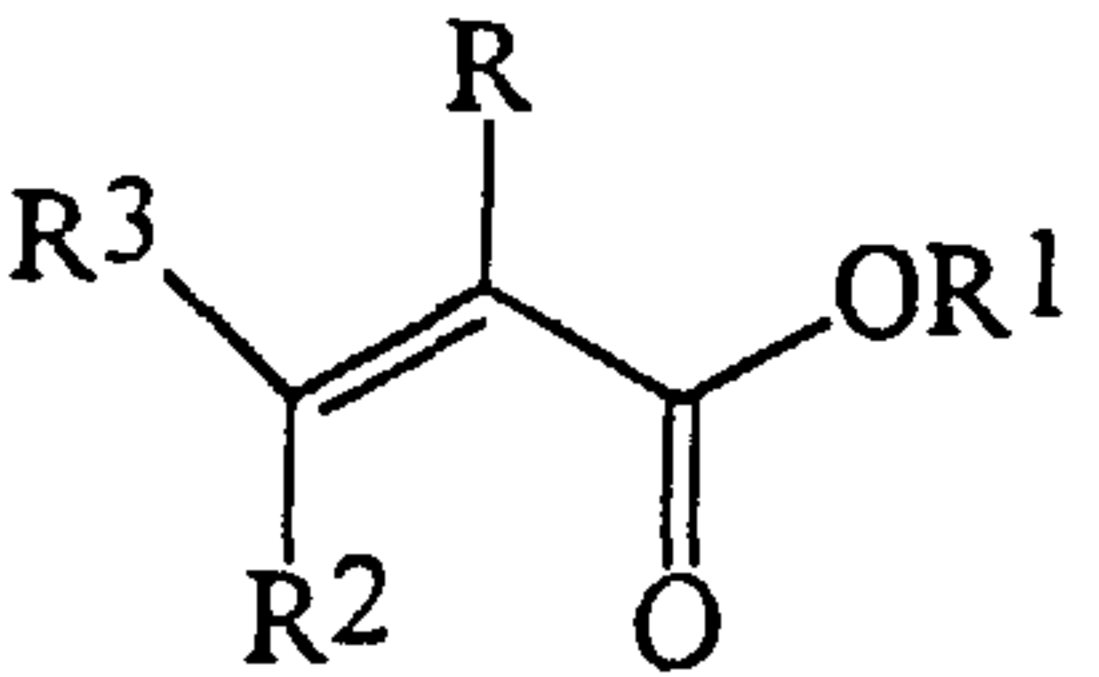
11. Biodiesel fuel containing gradient copolymers according to one or more of Claims 1 to 5.

12. Biodiesel fuel according to Claim 11, characterized in that the gradient copolymer according to one or more of Claims 1 to 5 is present in an amount in the range of 0.01 to 10 wt.-%, particularly 0.01 to 2 wt.-%.

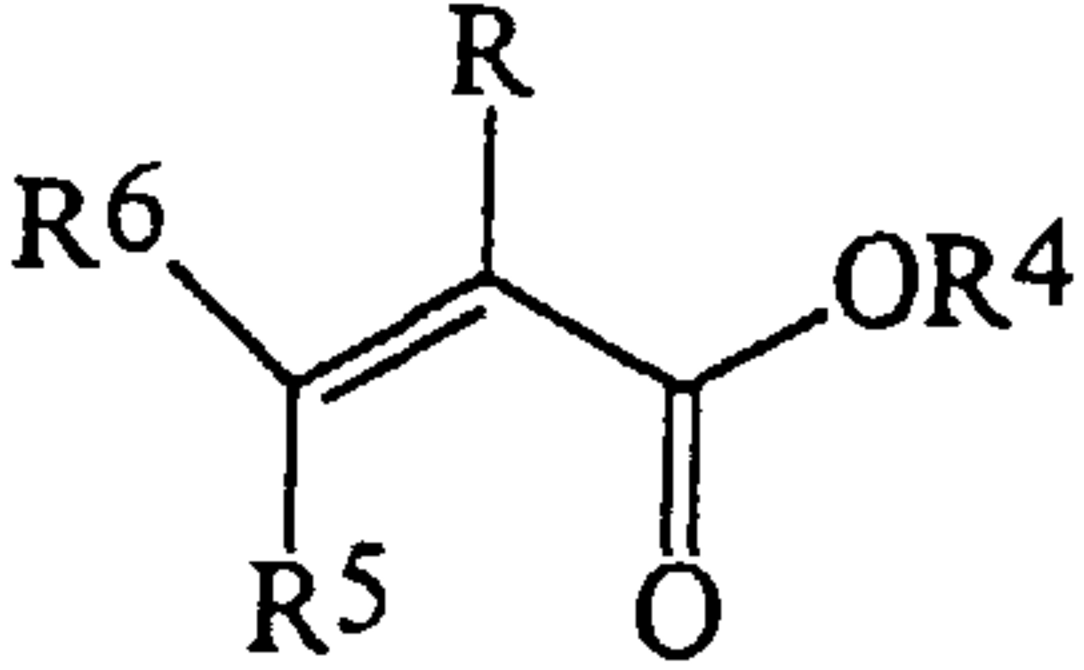
13. Process for the production of gradient copolymers according to one or more of Claims 1 to 5, characterized in that the olefin-unsaturated monomers are polymerized using initiators that have a transferable atom group, and one or more

catalysts that include at least one transition metal, in the presence of ligands that can form a coordination compound with the metallic catalyst(s).

14. Use of the copolymers according to one or more of Claims 1 to 5 as pour-point-improving agents or flow-improving agents.



(I)



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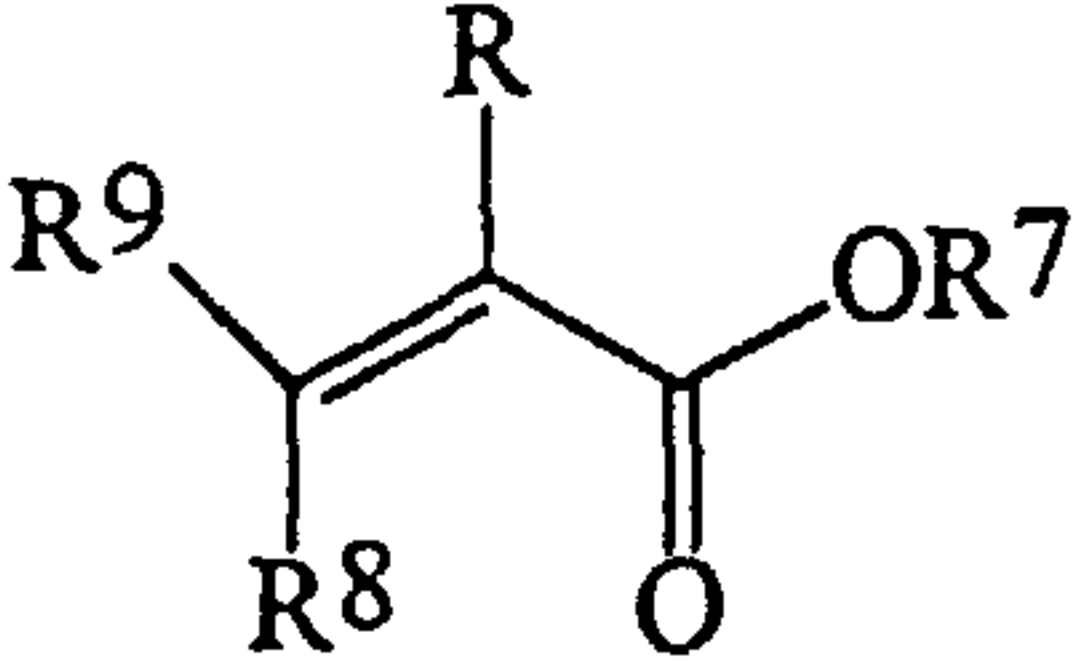

(III)