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(54) **Title:**

COPOLYMERS COMPRISING ESTER GROUPS AND USE THEREOF IN LUBRICANTS

(57) **Abstract:**

201000398 Foreign countries - 45 - Abstract The present invention relates to copolymers comprising ester groups and having at least one nonpolar segment P and at least one polar segment D, the polar segment D having at least 8 5 repeat units and the proportion by weight of dispersing repeat units in the polar segment D being at least 30%, based on the weight of the polar segment D, wherein the copolymer comprising ester groups is obtainable by NMP (nitroxide mediated polymerization). The invention further relates to lubricant oils having improved friction properties and comprising said copolymers.

Abstract

The present invention relates to copolymers comprising ester groups and having at least one nonpolar segment P and at least one polar segment D, the polar segment D having at least 8 repeat units and the proportion by weight of dispersing repeat units in the polar segment D being at least 30%, based on the weight of the polar segment D, wherein the copolymer comprising ester groups is obtainable by NMP (nitroxide mediated polymerization).
The invention further relates to lubricant oils having improved friction properties and comprising said copolymers.

Copolymers comprising ester groups and use thereof in lubricants

The present invention relates to copolymers comprising ester groups and to lubricants comprising these copolymers. The present invention further describes the use of copolymers comprising ester groups for improving the friction properties of lubricants.

For reasons of fuel economy, a task being addressed in modern research is that of reducing churning loss and internal friction of oils to an ever greater degree. As a result, there has been a trend in the last few years toward ever lower viscosities of the oils used and hence ever thinner lubricant films, especially at high temperatures. Accordingly, there is a constant search for solutions which compensate for the associated disadvantages.

WO 2004/087850 (Evonik RohMax) describes the film-forming, friction-reducing effect of PAMA block polymers in lubricant oils, for example block polymers based on 2-(4-morpholinyl)ethyl methacrylate MoEMA or based on 2-hydroxyethyl methacrylate (HEMA).

WO 2006/105926 (Evonik RohMax) describes a group of new monomers, for example 2-acetoacetoxyethyl methacrylate (AcAcEMA) and N-(2-methacryloyloxyethyl)ethyleneurea (EUMA; *ethylene urea methacrylate*), and the random and block copolymers derived therefrom and the use thereof in lubricant oils.

WO 2009/019065 (Evonik RohMax) describes sequential block or graft polymers having film-forming properties for use as an antifatigue additive.

Two Arkema documents describe block polymers which are obtainable via NMP (nitroxide mediated polymerization) and the use thereof in lubricant oils. WO 2005/056739 describes use as viscosity index improvers, while EP 1 696 020 describes use as pour point improvers. Similarly to the latter document, WO 2009/077396 (Ciba) describes block polymers obtainable via NMP for use as biodiesel flow improvers.

The above-detailed polymers already lead to a significant improvement in the friction properties of lubricant oils. However, there is a constant need to improve the profile of properties of lubricants, especially lubricant oils.
In view of the prior art, it is thus an object of the present invention to provide an additive or a lubricant, preferably a lubricant oil, having an improved profile of properties.

For example, the intention was to provide high-efficacy additives which lead to a significant improvement in the coefficient of friction of lubricants, especially lubricant oils.

In this context, this improvement is to be achieved under different conditions, more particularly also within the range of boundary lubrication or boundary friction, in which the surfaces are effectively in real contact, meaning that the separation of the surfaces is lower than the surface roughness thereof – a state which is attained especially at low speeds, low viscosities and/or high stresses. Such a state exists, for example, on piston changeover in the engine, and is simulated inter alia by the high frequency reciprocating rig (HFRR) test. On this topic, see also: *B.J. Hamrock; B.O. Jacobson; S.R. Schmid: Fundamentals of Fluid Film Lubrication, Marcel Dekker, New York, 2nd Ed., 2004.*

Moreover, the additives were to be particularly inexpensive to produce. It was therefore a further object of the present invention to provide additives which have high dispersibility, high corrosion protection (i.e. a high level of metal deactivator properties), high stability against oxidation and thermal stress, and high shear strength. In addition, the additives were also to be soluble in large amounts even in very nonpolar lubricant oils, for example in fully synthetic oils. It was a further object of the present invention to provide additives which, as well as friction-reducing action, additionally improve the flow properties of the lubricant oil, i.e. have a viscosity index-improving action. Moreover, the additives were to exhibit efficacy as an antiwear additive and/or as an antifatigue additive.

A distinction is made here between two groups of defects on the metallic surfaces of transmission systems, especially on gearings and roller bearings:

1. Wear resulting from continuous surface material removal or scuffing as a result of abrupt material removal after surface wear of both friction partners.
2. Fatigue which becomes visible through gray staining (surface fatigue, micro-pitting) or craters (sub-surface fatigue, pitting). This damage is caused by flaking-off or breaking-out of material owing to cracks, which are caused 20-40 µm or 100-500 µm below the surface by shear stresses in the metal lattice.

These objects, and further objects which are not stated explicitly but are immediately derivable or discernible from the connections discussed herein by way of introduction, are achieved by copolymers having all the features of claim 1. Appropriate modifications of the inventive copolymers are protected in the claims referring back to claim 1.

The present invention accordingly provides a copolymer comprising ester groups and having at least one nonpolar segment P and at least one polar segment D, the polar segment D having at least 8 repeat units and the proportion by weight of dispersing repeat units in the polar segment D being at least 30%, based on the weight of the polar segment D, which is characterized in that the copolymer comprising ester groups is obtainable by NMP (nitroxide mediated polymerization).

It is thus possible in an unforeseeable manner to provide an additive for lubricants, especially lubricant oils, which exhibit a particularly favorable profile of properties. For instance, the inventive copolymers lead to lubricant oils having outstanding friction properties. This improvement can surprisingly be achieved over a wide frequency range. As a result, these copolymers protect surfaces from wear.

Moreover, the use of the present copolymers can give a reduction in material fatigue (antifatigue additive). At the same time, these additives achieve a decrease in the above-detailed formation of gray staining (surface fatigue, micro-pitting) or craters (sub-surface fatigue, pitting).

Furthermore, these additives can be prepared in a simple and inexpensive manner, and it is possible to use commercially available components in particular. At the same time, production is possible on the industrial scale, without new plants or plants of complex construction being required for that purpose.

For instance, the polymers can be configured so as to be surprisingly shear-stable, such that the lubricants have a very long service life. In addition, the additive for use in accordance with the invention may bring about a multitude of desirable properties in the lubricant. For example, it is possible to produce lubricants with outstanding low-temperature properties or viscosity properties, which comprise the present polymers comprising ester groups. This allows the number of different additives to be minimized. Furthermore, the present polymers comprising ester groups are compatible with many additives. This allows the lubricants to be adjusted to a wide variety of different requirements.

The copolymers of the present invention exhibit excellent dispersion properties. As a result, these copolymers prevent any formation of deposits. The copolymers provide excellent anticorrosion properties, i.e. metal deactivator properties. The inventive copolymers have excellent binding of metal ions. This reduces premature oxidation of lubricant oils.

Furthermore, the additives for use do not exhibit any adverse effects on fuel consumption or the environmental compatibility of the lubricant.

Polymers comprising ester groups are understood in the context of the present invention to mean polymers obtainable by polymerizing monomer compositions which comprise ethylenically unsaturated compounds having at least one ester group, which are referred to hereinafter as ester monomers. Accordingly, these polymers contain ester groups as part of the side chain. These polymers include especially polyalkyl (meth)acrylates (PAMA), polyalkyl fumarates and/or polyalkyl maleates.

Ester monomers are known per se. They include especially (meth)acrylates, maleates and fumarates, which may have different alcohol radicals. The expression "(meth)acrylates" encompasses methacrylates and acrylates, and mixtures of the two. These monomers are widely known.

The polymer comprising ester groups comprises preferably at least 40% by weight, more preferably at least 60% by weight, especially preferably at least 80% by weight and most preferably at least 90% by weight of repeat units derived from ester monomers.

Inventive copolymers comprise at least one nonpolar segment P and at least one polar segment D, said polar segment D having at least 8 repeat units and the proportion by weight of dispersing repeat units in the polar segment D being at least 30%, based on the weight of the polar segment D.

The term "repeat unit" is widely known in the technical field. The present polymers are obtained by means of free-radical polymerization of monomers by the NMP process. This opens up double bonds to form covalent bonds. Accordingly, the repeat unit arises from the monomers used.

The inventive polymers have polar and nonpolar segments. The term "segment" in this context denotes a section of the polymer. The segments may have an essentially constant composition composed of one or more monomer units. In addition, the segments may have a gradient, in which case the concentration of different monomer units (repeat units) varies over the segment length. The polar segments D differ from the nonpolar segments P via the proportion of dispersing monomers. The nonpolar segments may have at most a small proportion of dispersing repeat units (monomer units), whereas the polar segments comprise a high proportion of dispersing repeat units (monomer units).

Dispersing monomers are understood to mean especially monomers with functional groups, for which it can be assumed that polymers with these functional groups can keep particles, especially soot particles, in solution (cf. R.M. Mortier, S.T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2nd ed. 1997). These include especially monomers which have boron-, phosphorus-, silicon-, sulfur-, oxygen- and nitrogen-containing groups, preference being given to oxygen- and nitrogen-functionalized monomers.

The polar segments D comprise, in accordance with the invention, at least 8, preferably at least 12 and most preferably at least 15 repeat units. At the same time, the polar segments D comprise at least 30% by weight, preferably at least 40% by weight, of dispersing repeat units, based on the weight of the polar segment D. In addition to the dispersing repeat units, the polar segment may also have repeat units which do not have any dispersing effect. The polar segment may have a random structure, such that the different repeat units have a random distribution over the segment length. In addition, the polar segment may have a block structure or a structure in the form of a gradient, such that the non-dispersing repeat units and the dispersing repeat units within the polar segment have an inhomogeneous distribution.

The nonpolar hydrophobic segment P may comprise a small proportion of dispersing repeat units, which is preferably less than 20% by weight, more preferably less than 10% by weight and most preferably less than 5% by weight, based on the weight of the nonpolar segment P. In a particularly appropriate configuration, the nonpolar segment P comprises essentially no dispersing repeat units.

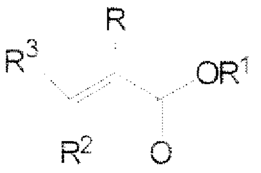
The nonpolar segment P of the polymer comprising ester groups may have 5 to 100% by weight, especially 20 to 98% by weight, preferably 30 to 95 and most preferably 70 to 92% by weight of repeat units derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical.

In a particular aspect, the nonpolar segment P of the polymer comprising ester groups may have 0 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of repeat units derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical.

In addition, the nonpolar segment P of the polymer comprising ester groups may have 0 to 40% by weight, preferably 0.1 to 30% by weight and more preferably 0.5 to 20% by weight of repeat units derived from ester monomers having 1 to 6 carbon atoms in the alcohol radical.

The nonpolar segment P of the polymer comprising ester groups comprises preferably at least 40% by weight, more preferably at least 60% by weight, especially preferably at least 80% by weight and most preferably at least 90% by weight of repeat units derived from ester monomers.

Mixtures from which the nonpolar segments P of the inventive polymers comprising ester groups are obtainable may contain 0 to 40% by weight, especially 0.1 to 30% by weight and more preferably 0.5 to 20% by weight of one or more ethylenically unsaturated ester compounds of the formula (I)



(I)

in which R is hydrogen or methyl, R^1 is a linear or branched alkyl radical having 1 to 6 carbon atoms, R^2 and R^3 are each independently hydrogen or a group of the formula -COOR' in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms.

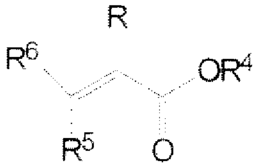
Examples of component (I) include

(meth)acrylates, fumarates and maleates which derive 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, hexyl (meth)acrylate;

cycloalkyl (meth)acrylates such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, such as 2-propynyl (meth)acrylate, allyl (meth)acrylate and vinyl (meth)acrylate.

The compositions to be polymerized to prepare the nonpolar segments P preferably contain 5 to 100% by weight, preferably 10 to 98% by weight and especially preferably 20 to 95% by weight of one or more ethylenically unsaturated ester compounds of the formula (II)



(II)

in which R is hydrogen or methyl, R^4 is a linear or branched alkyl radical having 7 to 15 carbon atoms, R^5 and R^6 are each independently hydrogen or a group of the formula -COOR'' in which R'' is hydrogen or an alkyl group having 7 to 15 carbon atoms.

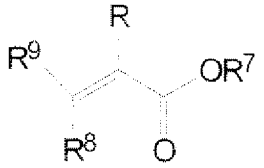
Examples of component (II) include:

(meth)acrylates, fumarates and maleates which derive from saturated alcohols, such as 2-ethylhexyl (meth)acrylate, heptyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, octyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, for example oleyl (meth)acrylate;

cycloalkyl (meth)acrylates, such as 3-vinylcyclohexyl (meth)acrylate, bornyl (meth)acrylate; and the corresponding fumarates and maleates.

In addition, preferred monomer compositions for preparing the nonpolar segments P comprise 0 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of one or more ethylenically unsaturated ester compounds of the formula (III)



(III)

in which R is hydrogen or methyl, R^7 is a linear or branched alkyl radical having 16 to 40, preferably 16 to 30, carbon atoms, R^8 and R^9 are each independently hydrogen or a group of the formula -COOR''' in which R''' is hydrogen or an alkyl group having 16 to 40, preferably 16 to 30, carbon atoms.

Examples of component (III) include (meth)acrylates which derive from saturated alcohols, such as hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate;

cycloalkyl (meth)acrylates such as 2,4,5-tri-t-butyl-3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-t-butylcyclohexyl (meth)acrylate;

and the corresponding fumarates and maleates.

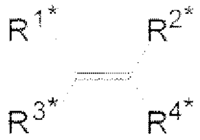
The ester compounds with a long-chain alcohol radical, especially components (II) and (III), can be obtained, for example, by reacting (meth)acrylates, fumarates, maleates and/or the corresponding acids with long-chain fatty alcohols, which generally gives a mixture of esters,

for example (meth)acrylates with different long-chain alcohol radicals. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900, Oxo Alcohol® 1100; Alfol® 610, Alfol® 810, Lial® 125 and Nafol® types (Sasol); Alphanol® 79 (ICI); Epal® 610 and Epal® 810 (Afton); Linevol® 79, Linevol® 911 and Neodol® 25E (Shell); Dehydad®, Hydrenol® and Lorol® types (Cognis); Acropol® 35 and Exxal® 10 (Exxon Chemicals); Kalcol® 2465 (Kao Chemicals).
Among the ethylenically unsaturated ester compounds, the (meth)acrylates are particularly preferred over the maleates and fumarates, i.e. R^2, R^3, R^5, R^6, R^8 and R^9 of the formulae (I), (II) and (III) are each hydrogen in particularly preferred embodiments.

If a mixture of ester monomers of formula (II) and ester monomers of formula (III) is used to produce the inventive copolymers, the weight ratio of ester monomers of the formula (II) to the ester monomers of the formula (III) may be within a wide range. The ratio of ester compounds of the formula (II) which have 7 to 15 carbon atoms in the alcohol radical to the ester compounds of the formula (III) which have 16 to 40 carbon atoms in the alcohol radical is preferably in the range from 50:1 to 1:30, more preferably in the range from 10:1 to 1:3, especially preferably 5:1 to 1:1.

In addition, the monomer mixture for preparing the nonpolar segments may comprise ethylenically unsaturated monomers which can be copolymerized with the ethylenically unsaturated ester compounds of the formulae (I), (II) and/or (III).

Particularly suitable comonomers for polymerization according to the present invention are those which correspond to the formula:



in which R^{1*} and R^{2*} are each independently selected from the group consisting of hydrogen, halogens, CN, linear or branched alkyl groups having 1 to 20, preferably 1 to 6 and more preferably 1 to 4, carbon atoms, which may be substituted by 1 to (2n+1) halogen atoms, where n is the number of carbon atoms of the alkyl group (for example CF_3), α,β-unsaturated linear or branched alkenyl or alkynyl groups having 2 to 10, preferably 2 to 6 and more preferably 2 to 4 carbon atoms, which may be substituted by 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the alkyl group, for example CH_2=CCl-, cycloalkyl groups having 3 to 8 carbon atoms, which may be substituted by 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the cycloalkyl group; aromatic or heteroaromatic groups having 3 to 40, preferably 5 to 18, carbon atoms which may be substituted by the groups detailed above, preferably alkyl groups having 1 to 6 carbon atoms or halogens; $C(=Y^*)R^{5*}$, $C(=Y^*)NR^{6*}R^{7*}$, $Y^*C(=Y^*)R^{5*}$, 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 may be quaternized with an additional R^{8*}, aryl or heterocyclyl group, where Y^* may be NR^{8*}, S or O, preferably O; R^{5*} is an alkyl group having 1 to 20 carbon atoms, an alkylthio having 1 to 20 carbon atoms, OR^{15} (R^{15} is hydrogen or an alkali metal), alkoxy of 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^{6*} and R^{7*} are each independently hydrogen or an alkyl group having 1 to 20 carbon atoms, or R^{6*} and R^{7*} together may form an alkylene group having 2 to 7 and preferably 2 to 5 carbon atoms, in which case they form a 3- to 8-membered and preferably 3- to 6-membered ring, and R^{8*} is hydrogen, linear or branched alkyl or aryl groups having 1 to 20 carbon atoms;

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

The preferred comonomers include

vinyl halides, for example vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;

styrene monomers, for example styrene, substituted styrenes having an alkyl substituent in the side chain, for example α-methylstyrene and α-ethylstyrene, substituted styrenes having an alkyl substituent on the ring, such as vinyltoluene and p-methylstyrene, halogenated styrenes, for example monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;

vinyl and isoprenyl ethers;

maleic acid and maleic acid derivatives different from those mentioned under (I), (II) and (III), for example maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide;

fumaric acid and fumaric acid derivatives different from those mentioned under (I), (II) and (III).

In addition, monomer mixtures for preparing the nonpolar segments may comprise dispersing monomers.

The proportion of comonomers is preferably 0 to 50% by weight, more preferably 0.1 to 40% by weight and most preferably 0.5 to 20% by weight, based on the weight of the monomer composition for preparing the nonpolar segment P.

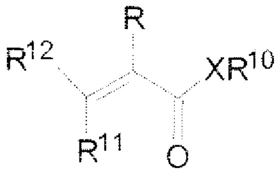
In a particularly preferred embodiment, the nonpolar segment P comprises repeat units derived from methacrylates having preferably 7 to 40, more preferably 10 to 30, carbon atoms in the alkyl radical, and repeat units derived from styrene monomers. The proportion of styrene monomers is preferably 0 to 40% by weight, more preferably 0.1 to 20% by weight and most preferably 0.5 to 5% by weight, based on the weight of the monomer composition for preparation of the nonpolar segment P. The proportion of methacrylates is preferably at least 60% by weight, more preferably at least 80% by weight and most preferably at least 90% by weight, based on the weight of the monomer composition for preparation of the nonpolar segment P.

In a further embodiment, the nonpolar segment P comprises repeat units derived from methacrylates having preferably 7 to 40, more preferably 10 to 30, carbon atoms in the alkyl radical, and repeat units derived from acrylates having preferably 7 to 40, more preferably 10 to 30, carbon atoms in the alkyl radical. The proportion of acrylates having preferably 7 to 40, more preferably 10 to 30, carbon atoms in the alkyl radical is preferably 0 to 40% by weight, more preferably 0.1 to 20% by weight and most preferably 0.5 to 5% by weight, based on the weight of the monomer composition for preparation of the nonpolar segment P. The proportion of methacrylates is preferably at least 60% by weight, more preferably at least

80% by weight and most preferably at least 90% by weight, based on the weight of the monomer composition for preparation of the nonpolar segment P.

In addition to the nonpolar segment P, a polymer usable in accordance with the invention comprises at least one polar segment D which comprises repeat units derived from dispersing monomers.

Dispersing monomers have been used for some time for functionalizing polymeric additives in lubricant oils, and are therefore known to those skilled in the art (cf. R.M. Mortier, S.T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2nd ed. 1997). Appropriately, it is possible to use especially heterocyclic vinyl compounds and/or ethylenically unsaturated, polar ester compounds of the formula (IV)



(IV)

in which R is hydrogen or methyl, X is oxygen, sulfur or an amino group of the formula -NH- or –NR^a- in which R^a is an alkyl radical having 1 to 40 and preferably 1 to 4 carbon atoms, R^{10} is a radical which comprises 2 to 1000, especially 2 to 100 and preferably 2 to 20 carbon atoms and has at least one heteroatom, preferably at least two heteroatoms, R^{11} and R^{12} are each independently hydrogen or a group of the formula –$COX'R^{10'}$ in which X' is oxygen or an amino group of the formula -NH- or –$NR^{a'}$- in which $R^{a'}$ is an alkyl radical having 1 to 40 and preferably 1 to 4 carbon atoms, and $R^{10'}$ is a radical comprising 1 to 100, preferably 1 to 30 and more preferably 1 to 15 carbon atoms, as dispersing monomers.

The expression "radical comprising 2 to 1000 carbon" denotes radicals of organic compounds having 2 to 1000 carbon atoms. Similar definitions apply for corresponding terms. It encompasses aromatic and heteroaromatic groups, and alkyl, cycloalkyl, alkoxy, cycloalkoxy, alkenyl, alkanoyl, alkoxycarbonyl groups, and also heteroaliphatic groups. The groups mentioned may be branched or unbranched. In addition, these groups may have customary substituents. Substituents are, for example, linear and branched alkyl groups having 1 to 6 carbon atoms, for example methyl, ethyl, propyl, butyl, pentyl, 2-methylbutyl or hexyl; cycloalkyl groups, for example cyclopentyl and cyclohexyl; aromatic groups such as phenyl or naphthyl; amino groups, hydroxyl groups, ether groups, ester groups and halides.

According to the invention, aromatic groups denote radicals of mono- or polycyclic aromatic compounds having preferably 6 to 20 and especially 6 to 12 carbon atoms. Heteroaromatic groups denote aryl radicals in which at least one CH group has been replaced by N and/or at least two adjacent CH groups have been replaced by S, NH or O, heteroaromatic groups having 3 to 19 carbon atoms.

Aromatic or heteroaromatic groups preferred in accordance with the invention derive from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenyl sulfone, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 2,5-diphenyl-1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 2,5-diphenyl-1,3,4-triazole, 1,2,5-triphenyl-1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, bipyridine, pyrazine, pyrazole, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or quinolizine, 4H-quinolizine, diphenyl ether, anthracene, benzopyrrole, benzoxathiadiazole, benzoxadiazole, benzopyridine, benzopyrazine, benzopyrazidine, benzopyrimidine, benzotriazine, indolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, aciridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridizine, benzopteridine, phenanthroline and phenanthrene, each of which may also optionally be substituted.

The preferred alkyl groups include the methyl, ethyl, propyl, isopropyl, 1-butyl, 2-butyl, 2-methylpropyl, tert-butyl radical, pentyl, 2-methylbutyl, 1,1-dimethylpropyl, hexyl, heptyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-decyl, 2-decyl, undecyl, dodecyl, pentadecyl and the eicosyl group.

The preferred cycloalkyl groups include the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the cyclooctyl group, each of which is optionally substituted with branched or unbranched alkyl groups.

The preferred alkanoyl groups include the formyl, acetyl, propionyl, 2-methylpropionyl, butyryl, valeroyl, pivaloyl, hexanoyl, decanoyl and the dodecanoyl group.

The preferred alkoxycarbonyl groups include the methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, tert-butoxycarbonyl group, hexyloxycarbonyl, 2-methylhexyloxycarbonyl, decyloxycarbonyl or dodecyloxycarbonyl group.

The preferred alkoxy groups include alkoxy groups whose hydrocarbon radical is one of the aforementioned preferred alkyl groups.

The preferred cycloalkoxy groups include cycloalkoxy groups whose hydrocarbon radical is one of the aforementioned preferred cycloalkyl groups.

The preferred heteroatoms which are present in the R^{10} radical include oxygen, nitrogen, sulfur, boron, silicon and phosphorus, preference being given to oxygen and nitrogen.

The R^{10} radical comprises at least one, preferably at least two, preferentially at least three, heteroatoms.

The R^{10} radical in ester compounds of the formula (IV) preferably has at least 2 different heteroatoms. In this case, the R^{10} radical in at least one of the ester compounds of the formula (IV) may comprise at least one nitrogen atom and at least one oxygen atom.

Examples of ethylenically unsaturated, polar ester compounds of the formula (IV) include aminoalkyl (meth)acrylates, aminoalkyl (meth)acrylamides, hydroxyalkyl (meth)acrylates, heterocyclic (meth)acrylates and/or carbonyl-containing (meth)acrylates.

The hydroxyalkyl (meth)acrylates include
2-hydroxypropyl (meth)acrylate,
3,4-dihydroxybutyl (meth)acrylate,

2-hydroxyethyl (meth)acrylate,
3-hydroxypropyl (meth)acrylate,
2,5-dimethyl-1,6-hexanediol (meth)acrylate and
1,10-decanediol (meth)acrylate.

Appropriate carbonyl-containing (meth)acrylates include, for example,
2-carboxyethyl (meth)acrylate,
carboxymethyl (meth)acrylate,
oxazolidinylethyl (meth)acrylate,
N-(methacryloyloxy)formamide,
acetonyl (meth)acrylate,
2-acetoacetoxyethyl (meth)acrylate,
mono-2-(meth)acryloyloxyethyl succinate,
N-(meth)acryloylmorpholine,
N-(meth)acryloyl-2-pyrrolidinone,
N-(2-(meth)acryloyloxyethyl)-2-pyrrolidinone,
N-(3-(meth)acryloyloxypropyl)-2-pyrrolidinone,
N-(2-(meth)acryloyloxypentadecyl)-2-pyrrolidinone,
N-(3-(meth)acryloyloxyheptadecyl)-2-pyrrolidinone and
N-(2-(meth)acryloyloxyethyl)ethyleneurea.

The heterocyclic (meth)acrylates include

2-(1-imidazolyl)ethyl (meth)acrylate, 2-(4-morpholinyl)ethyl (meth)acrylate and
1-(2-(meth)acryloyloxyethyl)-2-pyrrolidone.

Of particular interest are additionally aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylate amides, for example
dimethylaminopropyl (meth)acrylate,
dimethylaminodiglycol (meth)acrylate,
dimethylaminoethyl (meth)acrylate,
dimethylaminopropyl(meth)acrylamide,
3-diethylaminopentyl (meth)acrylate and
3-dibutylaminohexadecyl (meth)acrylate.

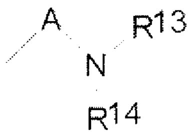
In addition, it is possible to use phosphorus-, boron- and/or silicon-containing (meth)acrylates to prepare the polar segments D, such as
2-(dimethylphosphato)propyl (meth)acrylate,
2-(ethylenephosphito)propyl (meth)acrylate,
dimethylphosphinomethyl (meth)acrylate,
dimethylphosphonoethyl (meth)acrylate,
diethyl(meth)acryloyl phosphonate,
dipropyl(meth)acryloyl phosphate, 2-(dibutylphosphono)ethyl (meth)acrylate,
2,3-butylene(meth)acryloylethyl borate,
methyldiethoxy(meth)acryloylethoxysilane,
diethylphosphatoethyl (meth)acrylate.

The preferred heterocyclic vinyl compounds include 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3 dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, N-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles, particular preference being given to using N-vinylimidazole and N-vinylpyrrolidone for functionalization.

The monomers detailed above can be used individually or as a mixture.

In a particular aspect of the present invention, at least one heteroatom in the R^{10} radical in at least one of the ester compounds of the formula (IV) may be separated from the X group via at least 4 atoms, more preferably via at least 6 atoms.

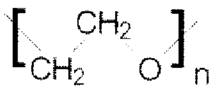
The R^{10} radical in at least one of the ester compounds of formula (IV) is preferably a group of the formula (V)



(V)

in which A is a joining group having 1 to 500 carbon atoms, preferably 1 to 100 carbon atoms and more preferably 1 to 50 carbon atoms, and the R^{13} and R^{14} radicals are each independently hydrogen or an alkyl group having 1 to 40 carbon atoms, more preferably 1 to 20 carbon atoms and most preferably 1 to 4 carbon atoms. The expression "joining group having 1 to 500 carbon atoms" denotes radicals of organic compounds comprising 1 to 500 carbon atoms. It comprises aromatic and heteroaromatic groups, and alkyl, cycloalkyl, alkoxy, cycloalkoxy, alkenyl, alkanoyl, alkoxycarbonyl groups, and heteroaliphatic groups. These radicals have been illustrated in detail above.

The preferred joining groups in formula (V) include groups of the formula (VI)

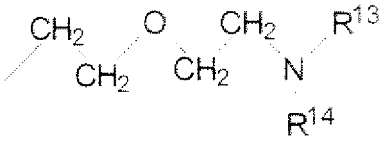


$$\left[\mathrm{CH_2{-}CH_2{-}O}\right]_n$$

(VI)

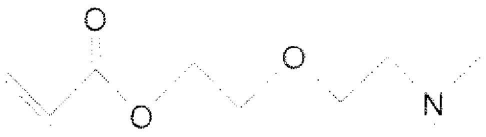
in which n is an integer in the range from 1 to 8, preferably 1 to 6 and more preferably 1 to 3.

The R^{10} radical in at least one ester compound of the formula (IV) is preferably a group of the formula (VII)



(VII).

More preferably, the dispersing monomer used may be dimethylaminodiglycol methacrylate (2-[2-(dimethylamino)ethoxy]ethyl methacrylate; 2-[2-(dimethylamino)ethoxy]ethyl 2-methyl-2-propenoate) of formula (VIII)

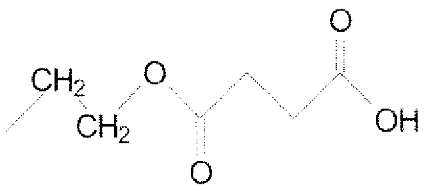


(VIII).

In a further aspect of the present invention, the R^{10} radical in at least one of the ester compounds of formula (IV) may comprise at least one group, more preferably at least two groups, of the formula -CO-. The groups of the formula –CO- may be carbonyl groups of ketones and/or aldehydes, carbonyl groups of carboxylic acids, carboxylic esters and/or carboxamides and/or carbonyl groups of carbonic acid derivatives, especially of urea groups and/or urethane groups.

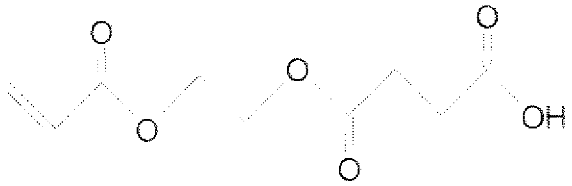
It is possible here for at least two groups of the formula -CO- to be joined to one another via not more than 4 atoms.

Preferably, the R^{10} radical in at least one ester compound of the formula (IV) may be a group of the formula (IX)



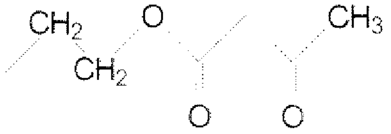
(IX).

More preferably, component d) comprises mono-2-methacryloyloxyethyl succinate of formula (X)



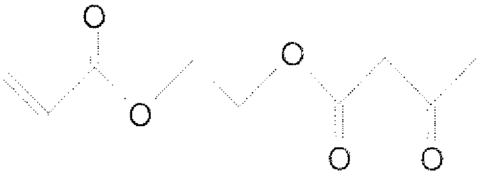
(X).

Preferably, the R^{10} radical in at least one ester compound of the formula (IV) may be a group of the formula (XI)



(XI).

More preferably, the dispersing monomer may be 2-acetoacetoxyethyl methacrylate 2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl 3-oxobutanoate) of formula (XII)

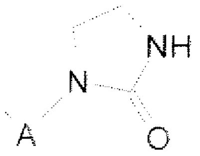


(XII).

In a further aspect of the present invention, the R^{10} radical in at least one of the ester compounds of formula (IV) may comprise at least one group of the formula -CO- and at least one nitrogen atom.

In this case, the R^{10} radical in at least one of the ester compounds of formula (IV) may have at least one urea group, and urea groups can generally be illustrated by the formula $-NR^b-CO-NR^c-$ in which the R^b and R^c radicals are each independently hydrogen or a group having 1 to 40 carbon atoms, preferably 1 to 20 carbon atoms and more preferably 1 to 4 carbon atoms, or the R^b and R^c radicals may form a ring having 1 to 80 carbon atoms.

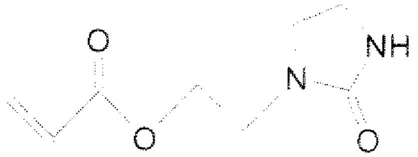
Preferably, the R^{10} radical in at least one ester compound of the formula (IV) may be a group of the formula (XIII)



(XIII)

in which A is a joining group having 1 to 500 carbon atoms, preferably 1 to 100 carbon atoms and more preferably 1 to 50 carbon atoms. The term "joining group having 1 to 500 carbon atoms" has been illustrated in detail above.

More preferably, the dispersing monomer used may be N-(2-methacryloyloxyethyl)ethyleneurea(2-(2-oxo-1-imidazolidinyl)ethyl 2-methyl-2-propenoate) of formula (XIV)



(XIV).

Of particular interest are especially polymers comprising ester groups which are obtained using 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, mono-2-methacryloyloxyethyl succinate, N-(2-methacryloyloxyethyl)ethyleneurea, 2-acetoacetoxyethyl methacrylate, 2-(4-morpholinyl)ethyl methacrylate, dimethylaminodiglycol methacrylate, dimethylaminoethyl methacrylate and/or dimethylaminopropylmethacrylamide, and the use of N-(2-methacryloyloxyethyl)ethyleneurea, 2-acetoacetoxyethyl methacrylate, 2-(4-morpholinyl)ethyl methacrylate is associated with particular advantages. In this context, very particular preference is given to 2-acetoacetoxyethyl methacrylate.

As well as the dispersing monomers, a composition for preparation of the polar segments may also comprise non-dispersing monomers which have been detailed above. These especially include ethylenically unsaturated ester compounds of the formulae (I), (II) and/or (III).

In a particularly preferred embodiment, the polar segment D comprises repeat units derived from dispersing methacrylates of formula (IV) and repeat units derived from styrene monomers. The proportion of styrene monomers is preferably 0 to 40% by weight, more preferably 0.1 to 30% by weight and most preferably 0.5 to 20% by weight, based on the weight of the monomer composition for preparation of the polar segment D. The proportion of dispersing methacrylates of formula (IV) is preferably at least 50% by weight, more preferably at least 70% by weight and most preferably at least 80% by weight, based on the weight of the monomer composition for preparation of the polar segment D.

In a particularly preferred embodiment, the polar segment D comprises repeat units derived from dispersing methacrylates of formula (IV) and repeat units derived from acrylates. The proportion of acrylates is preferably 0 to 40% by weight, more preferably 0.1 to 30% by weight and most preferably 0.5 to 20% by weight, based on the weight of the monomer composition for preparation of the polar segment D. The proportion of dispersing methacrylates of formula (IV) is preferably at least 50% by weight, more preferably at least 70% by weight and most preferably at least 80% by weight, based on the weight of the monomer composition for preparation of the polar segment D.

Appropriately, the weight ratio of the hydrophobic segments to the polar segments may be in the range from 100:1 to 1:1, more preferably in the range from 30:1 to 2:1 and most preferably in the range from 10:1 to 4:1.

The length of the hydrophobic and polar segments may vary within wide ranges. The nonpolar segments P preferably possess a weight-average degree of polymerization of at least 10, especially at least 40. The weight-average degree of polymerization of the hydrophobic segments is preferably in the range from 20 to 5000, especially from 50 to 2000.

The proportion of dispersing repeat units, based on the weight of the polymer comprising ester groups, is preferably in the range from 0.5% by weight to 20% by weight, more preferably in the range from 1.5% by weight to 15% by weight and most preferably in the range from 2.5% by weight to 10% by weight. At the same time, these repeat units preferably form a segment-like structure within the polymer comprising ester groups, such that preferably at least 70% by weight, more preferably at least 80% by weight, based on the total weight of the dispersing repeat units, are part of a polar segment D.

The proportion of repeat units derived from styrene monomers, based on the weight of the polymer comprising ester groups, may preferably be in the range from 0% by weight to 40% by weight, especially in the range from 0.1 to 25% by weight, more preferably in the range from 0.5% by weight to 10% by weight and most preferably in the range from 1% by weight to 5% by weight.

The present invention describes polymers which preferably have a high oil solubility. The term "oil-soluble" means that a mixture of a base oil and a polymer comprising ester groups is preparable without macroscopic phase formation, which has at least 0.1% by weight, preferably at least 0.5% by weight, of the polymers. The polymer may be present in dispersed and/or dissolved form in this mixture. The oil solubility depends especially on the proportion of the lipophilic side chains and on the base oil. This property is known to those skilled in the art and can be adjusted readily for the particular base oil via the proportion of lipophilic monomers.

Of particular interest, among others, are polymers which comprise ester groups and preferably have a weight-average molecular weight M_w in the range from 7500 to 1 000 000 g/mol, more preferably 10 000 to 600 000 g/mol and most preferably 15 000 to

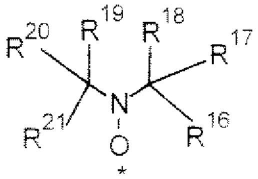
80 000 g/mol.

The number-average molecular weight M_n may preferably be in the range from 5000 to 800 000 g/mol, more preferably 7500 to 500 000 g/mol and most preferably 10 000 to 80 000 g/mol.

Additionally appropriate are polymers which comprise ester groups and whose polydispersity index M_w/M_n is in the range from 1 to 5, more preferably in the range from 1.05 to 4. The number-average and weight-average molecular weights can be determined by known processes, for example gel permeation chromatography (GPC).

The polymer comprising ester groups may have a variety of structures. For example, the polymer may be present as a diblock, triblock, multiblock, comb and/or star copolymer which has corresponding polar and nonpolar segments. According to the invention, the copolymer is obtainable by NMP (= nitroxide mediated polymerization). The NMP process is known to those skilled in the art and is described, for example, in K. Matyjaszewski, T. P. Davis, Handbook of Radical Polymerization, Wiley Interscience, Hoboken 2002.

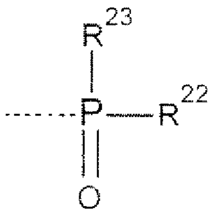
A characteristic feature of these processes is the presence of stable nitroxyl radical compounds, also called N-oxyl radical compounds, which are assumed to be able to react reversibly with the chain ends.
The particularly preferred nitroxyl radical compounds preferably include compounds of the structure (XV)



(XV)

in which R^{16}, R^{17}, R^{18}, R^{19}, R^{20} and R^{21} are each independently a radical comprising 1 to 100, preferably 1 to 30 and more preferably 1 to 15 carbon atoms, where two or more R^{16}, R^{17}, R^{18}, R^{19}, R^{20} and R^{21} radicals may form a ring, preferably a C_1-C_{10}-alkyl, C_1-C_{10}-alkenyl, C_1-C_{10}-alkoxy, C_6-C_{18}-aryl, C_7-C_{19}-aralkyl, C_6-C_{18}-aryl-C_1-C_8-alkyl or C_3-C_{18}-heteroaryl group, where the R^{18} and R^{19} radicals together may preferably form a ring, more preferably a (C_1-C_4)-alkylene bridge, which may be saturated or unsaturated, unsubstituted or substituted, especially by one or more substituents selected from a radical comprising 1 to 30 carbon atoms, C_1-C_8-amido, halogen, oxy, hydroxy, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylcarbonyloxy, arylcarbonyloxy, alkylcarbonylamino and arylcarbonylamino group. The R^{16}, R^{17}, R^{18}, R^{19}, R^{20} and R^{21} radicals here may contain heteroatoms which may be terminal or incorporated within the carbon chain. The particularly preferred heteroatoms include phosphorus atoms in particular. Accordingly, particularly preferred nitroxyl radical compounds have at least one phosphorus atom.

In a particular configuration of the present invention, at least one of the R^{16}, R^{17}, R^{18}, R^{19}, R^{20} and R^{21} radicals is a group of the formula (XVI)



$$\cdots\overset{\displaystyle R^{23}}{\underset{\displaystyle \| \atop O}{P}}-R^{22}$$

(XVI)

in which
the R^{22} and R^{23} radicals are each independently a halogen atom, especially a chlorine, bromine, fluorine or iodine atom, or a radical comprising 1 to 50, preferably 1 to 30 and more preferably 1 to 15 carbon atoms, preferably an alkyl, cycloalkyl, alkoxy, aryloxy, aryl, aralkyloxy, perfluoroalkyl, aralkyl having 1 to 20 carbon atoms; and the dotted line represents the bond of the group of formula (XVI) to the carbon atom bonded to the nitrogen atom of the N-oxide group.

The above-detailed nitroxyl radical compounds can be used individually or as a mixture.

The nitroxyl radical compounds used are preferably 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and/or the derivatives of 2,2,6,6-tetramethylpiperidine 1-oxyl substituted at the 4 position of the heterocycle, where the derivatives have one or more substituents selected from a radical comprising 1 to 30 carbon atoms, C_1-C_8-amido, halogen, oxy, hydroxy, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylcarbonyloxy, arylcarbonyloxy, alkylcarbonylamino and arylcarbonylamino groups, in which the radical comprising 1 to 30 carbon atoms is more preferably a $(C_1\text{-}C_{10})$-alkyl, $(C_1\text{-}C_{10})$-alkenyl, $(C_1\text{-}C_{10})$-alkoxy, $(C_6\text{-}C_{18})$-aryl, $(C_7\text{-}C_{19})$-aralkyl, $(C_6\text{-}C_{18})$-aryl-$(C_1\text{-}C_8)$-alkyl or $(C_3\text{-}C_{18})$-heteroaryl group.

More preferably, the following nitroxyl radical compounds are used: 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 4-methoxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-MeO-TEMPO), 4-oxo-2,2,6,6-tetramethylpiperidine 1-oxyl (4-oxo-TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-hydroxy-TEMPO), 4-benzoyloxy-2,2,6,6-tetramethylpiperidine 1-oxyl (BnO-TEMPO), 4-acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl, 4-acetamino-2,2,6,6-tetramethylpiperidine 1-oxyl (AA-TEMPO), 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl, N,N-dimethylamino-2,2,6,6-tetramethylpiperidine 1-oxyl (NNDMA-TEMPO), 3,6-dihydro-2,2,6,6-tetramethyl-1(2H)-pyridinyloxyl (DH-TEMPO), bis(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)sebacate, or a mixture of two or more of these compounds.

Very particular preference is given to nitroxyl radical compounds selected from:
N-tert-butyl-1-phenyl-2-methylpropyl N-oxide,
N-tert-butyl-1-(2-naphthyl)-2-methylpropyl N-oxide,
N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl N-oxide,
N-tert-butyl-1-dibenzylphosphono-2,2-dimethylpropyl N-oxide,
N-phenyl-1-diethylphosphono-2,2-dimethylpropyl N-oxide,
N-phenyl-1-diethylphosphono-1-methylethyl N-oxide,
N-1-(phenyl-2-methylpropyl)-1-diethylphosphono-1-methylethyl-N-oxide.

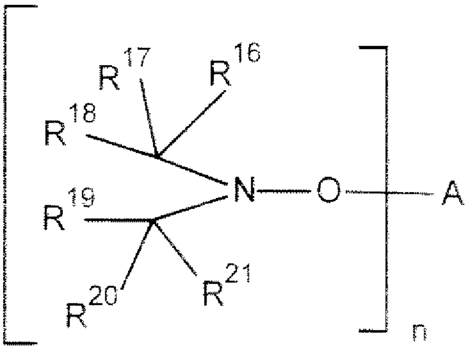
The stable free radical can be used in the reaction mixture of the polymerization or copolymerization in an amount of 0.005 to 5% by weight of the sum of the mass of polymerizable monomers and stable free radicals.

According to the method of polymerization, a separately added polymerization initiator can be used. These include the azo initiators widely known in the technical field, such as AIBN and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropyl-carbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned compounds with compounds which have not been mentioned but can likewise form free radicals.

The separately added polymerization initiator can be used in the customary amounts, though the amount of nitroxyl radical compounds must be sufficient to ensure controlled polymerization.

The nitroxyl radical compounds detailed above may, in a particular aspect, be used in the form of an initiator in the polymerization process, this releasing said nitroxyl radical compounds and at least one free-radical initiator.

The initiators which are usable with particular preference and can release said nitroxyl radicals include compounds of formula (XVII)



(XVII)

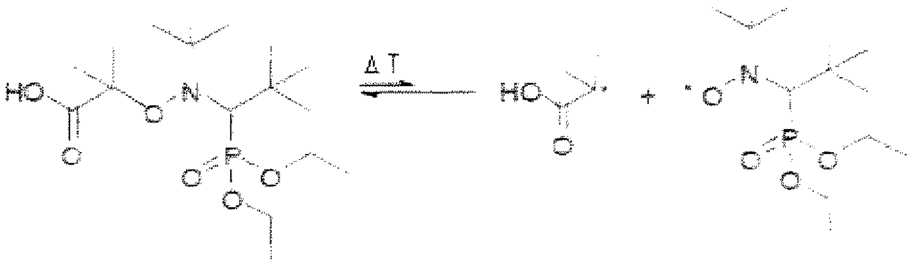
in which

the R^{16}, R^{17}, R^{18}, R^{19}, R^{20} and R^{21} radicals are each as defined above in formula (XV), n is an integer in the range from 1 to 10, preferably 1 to 5 and most preferably 1, and the A group is a radical comprising 1 to 50, preferably 1 to 30 and more preferably 1 to 15 carbon atoms. More preferably, the A group in formula (XVII) comprises at least one carboxylic acid, ester and/or cyano group and/or at least one halogen atom, preferably a fluorine atom. It is also possible here to use derivatives of the groups mentioned, for example salts.

Initiators which release the nitroxyl radical compounds mentioned are described, inter alia, in US 6,657,043, filed March 15, 2002 at the American Patent Office (USPTO) with application number 09/979,124; WO 2004/014926 A, filed July 23, 2003 at the French Patent Office with application number PCT/FR2003/002328; WO 00/49027 A, filed February 10, 2000 at the French Patent Office with application number PCT/FR00/00335; the initiators mentioned therein are incorporated into the present application for the purposes of disclosure.

The initiators mentioned which release both a free-radical initiator and a nitroxyl radical compound include especially hydroxylamine compounds, for example 2-methyl-2-(N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl-N-oxyl)propanoic acid, 2-methyl-2-(N-tert-butyl-1-dibenzylphosphono-2,2-dimethylpropyl-N-oxyl)propanoic acid, 2-methyl-2-(N-phenyl-1-diethylphosphono-2,2-dimethylpropyl-N-oxyl)propanoic acid, 2-methyl-2-(N-phenyl-1-diethylphosphono-1-methylethyl-N-oxyl)propanoic acid and/or 2-methyl-2-(N-1-(phenyl-2-methylpropyl)-1-diethylphosphono-1-methylethyl-N-oxyl)propanoic acid. The compounds mentioned can also be used as salts or propanoic esters, for example methyl esters.

A particularly preferred initiator (2-methyl-2-(N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl-N-oxyl)propanoic acid) which simultaneously provides both free-radical source/initiator and a nitroxyl radical in one molecule is available under the tradename BlocBuilder® MA:



In a preferred embodiment of the present invention, the copolymer is obtainable by a multistage polymerization, wherein a nonpolar segment P is produced in the first stage and a polar segment D in the last stage. More preferably, it is possible here to perform a multistage polymerization using a transferrable nitroxyl radical compound having at least one phosphorus atom, in such a way that the transferrable nitroxyl radical compound having at least one phosphorus atom is localized at the end of the polar segment D.

The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The polymerization temperature too is uncritical. However, it is generally in the range of -20° - 200°C, preferably 50° - 150°C and more preferably 80° - 130°C.

The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense. The solvent is selected according to the polarity of the monomers used, preference being given to using 100N oil, relatively light gas oil and/or aromatic hydrocarbons, for example toluene or xylene.

The inventive additives are used especially in lubricants, preferably lubricant oils, also referred to herein as lubricant oil compositions, in order to improve the friction properties thereof. Lubricant oils denote lubricants which are free-flowing at room temperature. These lubricants typically comprise a base oil. The preferred base oils include especially mineral oils, synthetic oils and natural oils.

Mineral oils are known per se and commercially available. They are generally obtained from mineral oil or crude oil by distillation and/or refining and optionally further purification and finishing processes, the term mineral oil including in particular the higher-boiling fractions of crude or mineral oil. In general, the boiling point of mineral oil is higher than 200°C, preferably higher than 300°C, at 5000 Pa. The production by low-temperature carbonization of shale oil, coking of bituminous coal, distillation of brown coal with exclusion of air, and also hydrogenation of bituminous or brown coal is likewise possible. Accordingly, mineral oils have, depending on their origin, different proportions of aromatic, cyclic, branched and linear hydrocarbons.

In general, a distinction is drawn between paraffin-base, naphthenic and aromatic fractions in crude oils or mineral oils, in which the term paraffin-base fraction represents longer-chain or highly branched isoalkanes, and naphthenic fraction represents cycloalkanes. In addition, mineral oils, depending on their origin and finishing, have different fractions of n-alkanes, isoalkanes having a low degree of branching, known as mono-methyl-branched paraffins, and compounds having heteroatoms, in particular O, N and/or S, to which a degree of polar properties are attributed. However, the assignment is difficult, since individual alkane molecules may have both long-chain branched groups and cycloalkane radicals, and aromatic parts. For the purposes of the present invention, the assignment can be effected to DIN 51 378, for example. Polar fractions can also be determined to ASTM D 2007.

The proportion of n-alkanes in preferred mineral oils is less than 3% by weight, the fraction of

O-, N- and/or S-containing compounds less than 6% by weight. The fraction of the aromatics and of the mono-methyl-branched paraffins is generally in each case in the range from 0 to 40% by weight. In one interesting aspect, mineral oil comprises mainly naphthenic and paraffin-base alkanes which have generally more than 13, preferably more than 18 and most preferably more than 20 carbon atoms. The fraction of these compounds is generally ≥ 60% by weight, preferably ≥ 80% by weight, without any intention that this should impose a restriction. A preferred mineral oil contains 0.5 to 30% by weight of aromatic fractions, 15 to 40% by weight of naphthenic fractions, 35 to 80% by weight of paraffin-base fractions, up to 3% by weight of n-alkanes and 0.05 to 5% by weight of polar compounds, based in each case on the total weight of the mineral oil.

An analysis of particularly preferred mineral oils, which was effected by means of conventional processes such as urea separation and liquid chromatography on silica gel, shows, for example, the following constituents, the percentages relating to the total weight of the particular mineral oil used:

n-alkanes having about 18 to 31 carbon atoms:
0.7-1.0%,

slightly branched alkanes having 18 to 31 carbon atoms:

1.0-8.0%,

aromatics having 14 to 32 carbon atoms:

0.4-10.7%,

iso- and cycloalkanes having 20 to 32 carbon atoms:

60.7-82.4%,

polar compounds:

0.1-0.8%,

loss:

6.9-19.4%.

An improved class of mineral oils (reduced sulfur content, reduced nitrogen content, higher viscosity index, lower pour point) results from hydrogen treatment of the mineral oils (hydroisomerization, hydrocracking, hydrotreatment, hydrofinishing). In the presence of hydrogen, this essentially reduces aromatic components and builds up naphthenic components.

Valuable information with regard to the analysis of mineral oils and a list of mineral oils which have a different composition can be found, for example, in T. Mang, W. Dresel (eds.): "Lubricants and Lubrication", Wiley-VCH, Weinheim 2001; R.M. Mortier, S.T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2nd ed. 1997; or J. Bartz: "Additive für Schmierstoffe", Expert-Verlag, Renningen-Malmsheim 1994.

Synthetic oils include organic esters, for example diesters and polyesters, polyalkylene glycols, polyethers, synthetic hydrocarbons, especially polyolefins, among which preference is given to polyalphaolefins (PAOs), silicone oils and perfluoroalkyl ethers. In addition, it is possible to use synthetic base oils originating from gas to liquid (GTL), coal to liquid (CTL) or biomass to liquid (BTL) processes. They are usually somewhat more expensive than the mineral oils, but have advantages with regard to their performance.

Natural oils are animal or vegetable oils, for example neatsfoot oils or jojoba oils.

Base oils for lubricant oil formulations are divided into groups according to API (American Petroleum Institute). Mineral oils are divided into group I (non-hydrogen-treated) and, depending on the degree of saturation, sulfur content and viscosity index, into groups II and III (both hydrogen-treated). PAOs correspond to group IV. All other base oils are encompassed in group V. Preferred lubricants preferably contain at least one base oil according to group II and/or III, more preferably according to group III, of the classification detailed above.

These base oils may also be used as mixtures and are in many cases commercially available.

The concentration of the polymers comprising ester groups in the lubricant oil composition is preferably in the range of 0.01 to 40% by weight, more preferably in the range of 0.5-25% by weight and most preferably in the range of 1-15% by weight, based on the total weight of the composition.

In addition to the polymers comprising ester groups for use in accordance with the invention, the lubricant oil compositions detailed here may also comprise further additives. These additives include VI improvers, pour point improvers and DI additives (dispersants, detergents, defoamers, corrosion inhibitors, antioxidants, antiwear and extreme pressure additives, friction modifiers).

The additionally usable VI improvers include especially polyalkyl (meth)acrylates having 1 to 30 carbon atoms in the alcohol group (PAMA; partly N/O-functional with advantageous additional properties as dispersants, antiwear additives and/or friction modifiers), which differ from the copolymers detailed in claim 1, and poly(iso)butenes (PIB), fumarate-olefin copolymers, styrene-maleate copolymers, hydrogenated styrene-diene copolymers (HSD) and olefin copolymers (OCP).

The pour point improvers include especially polyalkyl (meth)acrylates (PAMA) having 1 to 30 carbon atoms in the alcohol group.

Compilations of VI improvers and pour point improvers for lubricant oils are also detailed in T. Mang, W. Dresel (eds.): "Lubricants and Lubrication", Wiley-VCH, Weinheim 2001: R. M. Mortier, S. T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2nd ed. 1997; or J. Bartz: "Additive für Schmierstoffe", Expert-Verlag, Renningen-Malmsheim 1994.

Appropriate dispersants include poly(isobutylene) derivatives, e.g. poly(isobutylene)succinimides (PIBSIs); ethylene-propylene oligomers with N/O functionalities.

The preferred detergents include metal-containing compounds, for example phenoxides; salicylates; thiophosphonates, especially thiopyrophosphonates, thiophosphonates and phosphonates; sulfonates and carbonates. As metals, these compounds may comprise especially calcium, magnesium and barium. These compounds may be used preferably in neutral or overbased form.

Of particular interest are additionally defoamers, which are in many cases divided into silicone-containing and silicone-free defoamers. The silicone-containing defoamers include linear poly(dimethylsiloxane) and cyclic poly(dimethylsiloxane). The silicone-free defoamers which may be used are in many cases polyethers, for example poly(ethylene glycol) or tributyl phosphate.

In a particular embodiment, the inventive lubricant oil compositions may comprise corrosion inhibitors. These are in many cases divided into antirust additives and metal passivators/deactivators. The antirust additives used may, inter alia, be sulfonates, for example petroleumsulfonates or (in many cases overbased) synthetic alkylbenzenesulfonates, e.g. dinonylnaphthenesulfonates; carboxylic acid derivatives, for example lanolin (wool fat), oxidized paraffins, zinc naphthenates, alkylated succinic acids, 4-nonylphenoxy-acetic acid, amides and imides (N-acylsarcosine, imidazoline derivatives); amine-neutralized mono- and dialkyl phosphates; morpholine, dicyclohexylamine or diethanolamine. The metal passivators/deactivators include benzotriazole, tolyltriazole, 2-mercaptobenzothiazole, dialkyl-2,5-dimercapto-1,3,4-thiadiazole; N,N'-disalicylideneethylenediamine, N,N'-disalicylidenepropylenediamine; zinc dialkyldithiophosphates and dialkyl dithiocarbamates.

A further preferred group of additives is that of antioxidants. The antioxidants include, for example, phenols, for example 2,6-di-tert-butylphenol (2,6-DTB), butylated hydroxytoluene (BHT), 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol); aromatic amines, especially alkylated diphenylamines, N-phenyl-1-naphthylamine (PNA), polymeric 2,2,4-trimethyldihydroquinone (TMQ); compounds containing sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc dithiophosphates (ZnDTP), "OOS triesters" = reaction products of dithiophosphoric acid with activated double bonds from olefins, cyclopentadiene, norbornadiene, alpha-pinene, polybutene, acrylic esters, maleic esters (ashless on combustion); organosulfur compounds, for example dialkyl sulfides, diaryl sulfides, polysulfides, modified thiols, thiophene derivatives, xanthates, thioglycols, thio-aldehydes, sulfur-containing carboxylic acids; heterocyclic sulfur/nitrogen compounds, especially dialkyldimercaptothiadiazoles, 2-mercaptobenzimidazoles; zinc and methylene bis(dialkyldithiocarbamate); organophosphorus compounds, for example triaryl and trialkyl phosphites; organocopper compounds and overbased calcium- and magnesium-based phenolates and salicylates.

The preferred antiwear (AW) and extreme pressure (EP) additives include phosphorus compounds, for example trialkyl phosphates, triaryl phosphates, e.g. tricresyl phosphate, amine-neutralized mono- and dialkyl phosphates, ethoxylated mono- and dialkyl phosphates, phosphites, phosphonates, phosphines; compounds containing sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc C_{3-12}dialkyldithiophosphates (ZnDTPs), ammonium dialkyldithiophosphates, antimony dialkyldithiophosphates, molybdenum dialkyldithiophosphates, lead dialkyldithiophosphates, "OOS triesters" = reaction products of dithiophosphoric acid with activated double bonds from olefins, cyclopentadiene, norbornadiene, alpha-pinene, polybutene, acrylic esters, maleic esters, triphenylphosphorothionate (TPPT); compounds containing sulfur and nitrogen, for example zinc bis(amyl dithiocarbamate) or methylenebis(di-n-butyl dithiocarbamate); sulfur compounds containing elemental sulfur and H_2S-sulfurized hydrocarbons (diisobutylene, terpene); sulfurized glycerides and fatty acid esters; overbased sulfonates; chlorine compounds or solids such as graphite or molybdenum disulfide.

A further preferred group of additives is that of friction modifiers. The friction modifiers used may include mechanically active compounds, for example molybdenum disulfide, graphite (including fluorinated graphite), poly(trifluoroethylene), polyamide, polyimide; compounds which form adsorption layers, for example long-chain carboxylic acids, fatty acid esters, ethers, alcohols, amines, amides, imides; compounds which form layers through tribochemical reactions, for example saturated fatty acids, phosphoric acid and thiophosphoric esters, xanthogenates, sulfurized fatty acids; compounds which form polymer-like layers, for example ethoxylated dicarboxylic acid partial esters, dialkyl phthalates, methacrylates, unsaturated fatty acids, sulfurized olefins or organometallic compounds, for example molybdenum compounds (molybdenum dithiophosphates and molybdenum dithiocarbamates MoDTC) and their combinations with ZnDTPs, copper-containing organic compounds.

Some of the additives detailed above may fulfill multiple functions. ZnDTP, for example, is primarily an antiwear additive and extreme pressure additive, but also has the character of an antioxidant and corrosion inhibitor (here: metal passivator/deactivator).

The additives detailed above are described in more detail, inter alia, in T. Mang, W. Dresel (eds.): "Lubricants and Lubrication", Wiley-VCH, Weinheim 2001; J. Bartz: "Additive für Schmierstoffe", Expert-Verlag, Renningen-Malmsheim 1994; R.M. Mortier, S.T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2nd ed. 1997.

Preferred lubricant oil compositions have a viscosity, measured at 40°C to ASTM D 445, in the range of 10 to 120 mm^2/s, more preferably in the range of 20 to 100 mm^2/s. The kinematic viscosity KV_{100} measured at 100°C is preferably at least 3.5 mm^2/s, more preferably at least 4.0 mm^2/s and most preferably at least 4.5 mm^2/s.

In a particular aspect of the present invention, preferred lubricant oil compositions have a viscosity index determined to ASTM D 2270 in the range of 100 to 400, more preferably in the range of 125 to 325 and most preferably in the range of 150 to 250.

Appropriate lubricant oil compositions have a PSSI to DIN 51350-6 (20h, tapered roller bearing) less than or equal to 100. The PSSI is more preferably less than or equal to 65, especially preferably less than or equal to 25.

The present lubricant oil compositions can be used especially as a transmission oil, motor oil or hydraulic oil. Surprising advantages can be achieved especially when the present lubricants are used in manual, automated manual, double clutch or direct-shift gearboxes (DSG), automatic and continuous variable transmissions (CVCs). In addition, the present lubricants can be used especially in transfer cases and axle or differential gearings.

The present polymers comprising ester groups can additionally serve as antifatigue additives in lubricants. It has been found that, surprisingly, these additives counteract material fatigue, such that the lifetime of transmissions, engines or hydraulic systems can be increased. This finding can be established by various methods. The fatigue time (crater resistance) of the lubricant oil formulations can be determined either by methods for gearings or for roller bearings. The methods which follow cover a wide range of Hertzian pressures.

The fatigue time (number of rotations) can be determined, for example, on a standardized four-ball apparatus (FBA) to DIN 51350-1, in which a rotating ball under load is pressed onto three identical, likewise rotating balls. The test method employed is VW-PV-1444 of Volkswagen AG ("Grübchenfestigkeit von Bauteilen mit Wälzreibung - Pittingtest" [Crater resistance of components with rolling friction - pitting test], VW-PV-1444, Volkswagen AG).

The test temperature is 120°C. With a load of 4.8 kN and a rotational speed of 4000 rpm, the entrainment speed is 5.684 m/s at a maximum Hertzian pressure of 7.67 GPa. Fatigue occurs as soon as an acceleration sensor registers vibrations in the frequency band of the rollover frequencies of the test bodies greater than 0.25 *g* (acceleration due to gravity $g = 9.81 \text{ m/s}^2$). This typically indicates craters on the rolling path of diameter 1-2 mm. This test is referred to hereinafter as the FBA test.

In addition, fatigue can be determined by means of an FAG FE8 test. To this end, the FE8 roller bearing lubricant test rig to DIN 51819-1 from FAG (Schaeffler KG, Schweinfurt) can be used. Here, the fatigue time (in hours) of two cylindrical roller thrust bearings mounted together in each case is examined according to test method VW-PV-1483 ("Prüfung der Grübchentragfähigkeit in Wälzlagern - Ermüdungstest" [Testing of crater resistance in roller bearings - fatigue test], VW-PV-1483, Volkswagen AG, drafted September 2006; constituent of oil standards VW TL52512/2005 for manual transmissions and VW TL52182/2005 for double-clutch transmissions of Volkswagen AG). Bearing washers with an arithmetic roughness of 0.1-0.3 µm are used.

Measurement is effected at 120°C. With a load of 60 kN and a rotational speed of 500 rpm, the entrainment speed is 1.885 m/s at a maximum Hertzian pressure of 1.445 GPa. Fatigue occurs as soon as the torque (i.e. the moment of friction) has an increase by more than 10%, i.e. even in the case of fatigue only to one cylindrical roller thrust bearing.

In principle, the FE8 roller bearing lubricant test rig can also be operated according to the more severe ZF-702-232/2003 method of ZF Friedrichshafen AG (cf. "ZF Bearing Pitting Test", ZF-702-232, ZF Friedrichshafen AG, 2004).

The Unisteel Machine according to IP 305/79 based on a roller bearing with 11 balls (in modifications also only with 3 balls), which is widespread in industry, also offers a method of determining the fatigue time of bearings.

In addition, it is possible to use a gear rig test machine from FZG (Institute for Machine Elements - Gear Research Center of the Technical University of Munich) to DIN 51354-1. On this test machine, the fatigue time (in hours) is determined using specified PT-C (*pitting test type C*) gears. The method is described in FVA Information Sheet 2/IV (cf. U. Schedl: "FVA-Forschungsvorhaben 2/IV: Pittingtest - Einfluss der Schmierstoffs auf die Grübchenlebensdauer einsatzgehärteter Zahnräder im Einstufen- und Lastkollektivversuch", Forschungsvereinigung Antriebstechnik, Book 530, Frankfurt 1997; "Pittingtest - Einfluss der Schmierstoffs auf die Grübchenlebensdauer einsatzgehärteter Zahnräder im Einstufen- und Lastkollektivversuch", FVA Information Sheet 2/IV, Forschungsvereinigung Antriebstechnik, Frankfurt 1997).

Measurement is effected at 120°C. At load level 10 (i.e. a torque of 373 Nm) and a rotational speed of 1450 rpm, the entrainment speed is 5.678 m/s at a maximum Hertzian pressure of 1.834 GPa. Fatigue occurs when craters of total area >= 5 mm^2 are observed. This method is referred to hereinafter as FZG PT-C 10/120 test.

The utilization of the further-developed PTX-C test gearing, which is close to reality, in the FZG gear rig test machine to DIN 51354-1 leads to improved repeatability and comparability of the fatigue time. The method is described in FVA Information Sheet 371 (cf. T. Radev: "FVA-Forschungsvorhaben 371: Entwicklung eines praxisnahen Pittingtests", Forschungsvereinigung Antriebstechnik, Book 710, Frankfurt 2003; "Development of a Practice Relevant Pitting Test", FVA Information Sheet 371, Forschungsvereinigung Antriebstechnik, Frankfurt 2006).

Measurement is effected at 90°C. At load level 10 (i.e. a torque of 373 Nm) and a rotational speed of 1450 rpm, the entrainment speed is 5.678 m/s at a maximum Hertzian pressure of 2.240 GPa. Fatigue occurs when craters of total area >= 5 mm^2 are observed. This method is referred to hereinafter as FZG PTX-C 10/90 test.

The inventive lubricants exhibit excellent friction properties which can be demonstrated under a wide variety of different conditions. Accordingly, the present invention also provides for the use of the copolymers comprising ester groups for improvement of friction properties.

In a preferred aspect of the present invention, particularly the friction properties in the boundary lubrication range detailed above can be improved. This range is characterized by a surface separation R which is less than the surface roughness, this being given as the mean roughness Ra which can be measured by tactile methods (cf. DIN EN ISO 4287). The excellent friction properties can be determined inter alia by means of UTFI (Ultrathin Film Interferometry), MTM (Mini-Traction Machine) or HFRR (High Frequency Reciprocating Rig).

To determine the tribological properties by means of ultrathin film interferometry (UTFI), a steel ball which rolls under load on a coated glass pane is used. The change in the film thickness between ball and pane is studied as a function of rolling speed by optical interferometry.

The UTFI values can preferably be determined using the following test parameters: Young's modulus (AISI 52100 steel) = 210 GPa, Young's modulus (glass) = 75 GPa, root mean square (RMS) roughness (steel) = 10-13 nm, RMS roughness (glass) = 3 nm, load = 20 N, resulting maximum Hertzian pressure = 0.54 GPa, rolling or entrainment speed = 0.005-1.5 m/s, temperature = 120°C.

To determine the tribological properties by means of a mini-traction machine (MTM), a steel ball of diameter 19 mm is used, which slides or rolls on a polished steel sheet. The ball and sheet are driven independently by means of electric motors, such that different sliding/rolling ratios (SRR) can be established. The coefficient of friction is studied as a function of mean rolling speed. As a result of a friction experiment, Stribeck curves were obtained, from which the coefficients of friction are obtained.

The MTM values can preferably be determined using the following test parameters: Young's modulus (AISI 52100 steel) = 210 GPa, roughness (steel ball) = 10-13 nm, roughness (steel sheet) = 25-30 nm, load = 30 N, resulting maximum Hertzian pressure = 0.93 GPa, SSR=50%, mean rolling speed or entrainment speed = 0.005-2.5 m/s, temperature = 120°C.

To determine the tribological properties by means of a high frequency reciprocating rig (HFRR), a steel ball of diameter 6 mm is fixed in a clamp device and pressed under load onto the surface of a steel sheet of diameter 10 mm. The coefficient of friction is recorded continuously, and the wear scar diameter is determined at the end of the experiment.

The HFRR values can preferably be determined using the following test parameters: Young's modulus (AISI 52100 steel ball) = 210 GPa, hard VPN 800 steel sheets, rather than soft sheets typically used for fuel studies, load = 4 N, deflection = 2 mm, frequency = $20s^{-1}$, friction time = 75 min, temperature = 120°C.
In this test, the inventive polymers exhibit a surprisingly large improvement in the HFRR values. After a measurement for 75 minutes with the parameters detailed above, preferred lubricants exhibit a relative wear of not more than 0.8, preferably not more than 0.75 and more preferably not more than 0.65. The relative wear is based here on a comparable lubricant without the addition of the inventive additives. The absolute wear, measured as the wear scar diameter, is preferably not more than 280 µm, especially not more than 260 µm, more preferably not more than 240 µm and most preferably not more than 220 µm. In addition, preferred lubricants according to the HFRR test exhibit a friction value of not more than 0.2, especially not more than 0.15, more preferably not more than 0.10. Based on a comparable lubricant without the addition, the relative friction value is preferably at most 0.8, preferably at most 0.75 and more preferably at most 0.65 (relative friction value = friction value with copolymer/friction value of reference oil).

Accordingly, the present invention also provides for the use of the copolymers comprising ester groups for reducing wear.

Additionally of particular interest are lubricant oil compositions having a high-shear viscosity HTHS measured at 150°C of at least 1.6 mPas, more preferably at least 2.0 mPas. The high-shear viscosity HTHS measured at 100°C is preferably at most 10 mPas, more preferably at most 7 mPas and most preferably at most 5 mPas. The difference in the high-shear viscosities HTHS which are measured at 100°C and 150°C, $HTHS_{100} - HTHS_{150}$, is preferably at most 4 mPas, more preferably at most 3.3 mPas and most preferably at most 2.5 mPas. The ratio of high-shear viscosity at 100°C $HTHS_{100}$ to high-shear viscosity at 150°C $HTHS_{150}$, $HTHS_{100}/HTHS_{150}$, is preferably at most 2.0, more preferably at most 1.9. The high-shear viscosity HTHS can be measured at the respective temperature to ASTM D4683.

The present invention is to be illustrated hereinafter by examples and comparative examples, without any intention that this should impose a restriction.

Example 1

A reaction flask equipped with a heating mantle, internal temperature regulation, stirrer, nitrogen inlet and condenser is initially charged with 945 g of 12/15-alkyl methacrylate and 42 g of styrene. The mixture is degassed thoroughly with dry ice and heated to 80°C with introduction of nitrogen. During the heating phase, at 60°C, the polymerization is started by addition of 19 g of initiator (BlocBuilder® MA). Later, the conversion of the 12/15-alkyl methacrylate is monitored via the refractive index. After about 4 h, at a conversion of 90%, the degassed mixture of 52 g of hydroxyethyl methacrylate (HEMA) and 10 g of styrene is added. The reaction mixture is stirred at 80°C for a further 16 hours.

The weight-average molecular weight of the polymer, determined by means of GPC, was about 25 000 g/mol.

The properties of the polymer were examined in an HFRR test. For this purpose, a lubricant oil formulation was produced using a group III oil (NexBase 3030), and the kinematic viscosity at 120°C was adjusted to approx. 4.73 mm²/s. The concentration of the polymer was 13.3% by weight. The coefficient of friction determined by HFRR was 0.132. A group III reference oil composed of Nexbase 3080 + Nexbase 3060 having a kinematic viscosity at 120°C of 4.74 mm²/s exhibited a coefficient of friction of approx. 0.21.

Example 2

Example 1 is essentially repeated, except that the nonpolar segment P is prepared using an initial charge of 914 g of 12/15-alkyl methacrylate and 32 g of styrene. On attainment of 90% conversion, the polar segment D is then prepared by adding the degassed mixture of 84 g of N-(2-methacryloyloxyethyl)ethyleneurea (EUMA) and 21 g of styrene, and the reaction mixture is likewise stirred at 80°C for 16 hours.

The weight-average molecular weight of the polymer, determined by means of GPC, was about 25 000 g/mol.

The properties of the polymer were examined in an HFRR test. For this purpose, a lubricant oil formulation was produced using a group III oil (NexBase 3030), and the kinematic viscosity at 120°C was adjusted to approx. 4.70 mm²/s. The concentration of the polymer was 13.2% by weight. The coefficient of friction determined by HFRR was 0.096. A group III reference oil composed of Nexbase 3080 + Nexbase 3060 having a kinematic viscosity at 120°C of 4.74 mm²/s exhibited a coefficient of friction of approx. 0.21.

Example 3

Example 1 is essentially repeated, except that the nonpolar segment P is prepared using an initial charge of 914 g of 12/15-alkyl methacrylate and 42 g of styrene. On attainment of 90% conversion, the polar segment D is then prepared by adding the degassed mixture of 84 g of acetoacetoxyethyl methacrylate (AcAcEMA) and 11 g of styrene, and the reaction mixture is likewise stirred at 80°C for 16 hours.

The weight-average molecular weight of the polymer, determined by means of GPC, was about 25 000 g/mol.

The properties of the polymer were examined in an HFRR test. For this purpose, a lubricant oil formulation was produced using a group III oil (NexBase 3030), and the kinematic viscosity at 120°C was adjusted to approx. 4.74 mm²/s. The concentration of the polymer was 14.8% by weight. The coefficient of friction determined by HFRR was 0.085. A group III reference oil composed of Nexbase 3080 + Nexbase 3060 having a kinematic viscosity at 120°C of 4.74 mm²/s exhibited a coefficient of friction of approx. 0.21. In addition, the copolymer exhibited an absolute wear of approx. 208 µm, whereas the reference oil exhibited wear of approx. 334 µm.

Comparative example 1

A 2 l reaction flask equipped with a heating mantle, internal temperature regulation, stirrer, nitrogen inlet and condenser is initially charged with 900 g of isoC12-C15-alkyl methacrylate, 225 g of butyl acetate and 6.75 g of cumyl dithiobenzoate (initiator for RAFT). The mixture is thoroughly degassed with dry ice and heated to 90°C with introduction of nitrogen. On attainment of the reaction temperature, the polymerization is started by addition of 1.8 g of tBPO (tert-butyl per-2-ethylhexanoate). After four and eight hours of reaction time, 0.9 g of tBPO is added in each case and then the mixture is stirred for a further fifteen hours.

This is followed by the addition of 71.9 g of N-(2-methacryloyloxyethyl)ethyleneurea (EUMA) in 300 g of butyl acetate and 0.97 g of tBPO. After a further four hours, the mixture is diluted with 647.9 g of oil. Subsequently, the mixture is degassed on a rotary evaporator at 120°C and a final vacuum of 12 mbar.

The weight-average molecular weight of the polymer, determined by means of GPC, was about 75 000 g/mol.

The properties of the polymer were examined in an HFRR test. For this purpose, a lubricant oil formulation was produced using a group I oil (Enerpar 11 = 150N), and the kinematic viscosity at 120°C was adjusted to approx. 9.21 mm²/s. The concentration of the polymer was 7.0% by weight. The coefficient of friction determined by HFRR was 0.18. A group I reference oil composed of Ergenol BS + Esso 600N having a kinematic viscosity at 120°C of approx. 9.24 mm²/s exhibited a coefficient of friction of approx. 0.20.

Comparative example 2

A 2 l reaction flask equipped with a heating mantle, internal temperature regulation, stirrer, nitrogen inlet and condenser is initially charged with 900 g of isoC12-C15-alkyl methacrylate, 225 g of butyl acetate and 6.75 g of cumyl dithiobenzoate (initiator for RAFT). The mixture is thoroughly degassed with dry ice and heated to 85°C with introduction of nitrogen. On attainment of the reaction temperature, the polymerization is started by addition of 1.8 g of tBPO (tert-butyl per-2-ethylhexanoate). After five hours of reaction time, 0.9 g of tBPO is added. After a further five hours of reaction time, 78.3 g of acetoacetoxyethyl methacrylate (AcAcEMA) in 300 g of butyl acetate and 0.98 g of tBPO are added. Subsequently, the mixture is stirred at 85°C for a further 30 hours. Thereafter, the mixture is diluted with 526.8 g of oil and degassed on a rotary evaporator at 120°C and a final vacuum of 12 mbar.
The weight-average molecular weight of the polymer, determined by means of GPC, was about 150 000 g/mol.

The properties of the polymer were examined in an HFRR test. For this purpose, a lubricant oil formulation was produced using a group I oil (Enerpar 11 = 150N), and the kinematic viscosity at 120°C was adjusted to approx. 9.12 mm²/s. The concentration of the polymer was 5.5% by weight. The coefficient of friction determined by HFRR was 0.19. A group I reference oil composed of Ergenol BS + Esso 600N having a kinematic viscosity at 120°C of approx. 9.24 mm²/s exhibited a coefficient of friction of approx. 0.20.

Claims

1. A copolymer comprising ester groups and having at least one nonpolar segment P and at least one polar segment D, the polar segment D having at least 8 repeat units and the proportion by weight of dispersing repeat units in the polar segment D being at least 30%, based on the weight of the polar segment D, characterized in that the copolymer comprising ester groups is obtainable by NMP (nitroxide mediated polymerization).

2. A copolymer as claimed in at least one of the preceding claims, characterized in that the copolymer is obtainable by a multistage polymerization, with preparation of a nonpolar segment P in the first stage and of a polar segment D in the last stage.

3. A copolymer as claimed in at least one of the preceding claims, characterized in that the transferrable nitroxyl radical compound used in the for performance of the NMP comprises at least one phosphorus atom.

4. A copolymer as claimed in at least one of the preceding claims, characterized in that the copolymer is obtainable by a multistage polymerization in which a transferrable nitroxyl radical compound having at least one phosphorus atom is used, the transferrable nitroxyl radical compound having at least one phosphorus atom being localized at the end of the polar segment D.

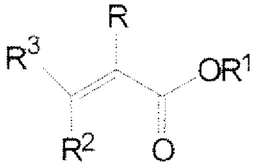
5. A copolymer as claimed in at least one of the preceding claims, characterized in that the copolymer comprises repeat units derived from styrene monomers and repeat units derived from a methacrylate.

6. A copolymer as claimed in at least one of the preceding claims, characterized in that the copolymer comprises repeat units derived from styrene monomers, and the proportion of repeat units derived from styrene monomers is in the range from 0.5 to 10% by weight.

7. A copolymer as claimed in at least one of the preceding claims, characterized in that the weight ratio of the nonpolar segments P to the polar segments D is in the range from 100:1 to 1:1.

8. A copolymer as claimed in at least one of the preceding claims, characterized in that the nonpolar segment P is obtainable by polymerization of a monomer composition comprising

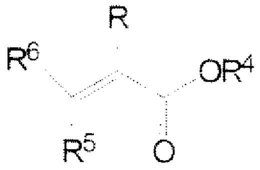
a) 0 to 40% by weight, based on the weight of the monomer composition for preparation of the nonpolar segments, of one or more ethylenically unsaturated ester compounds of the formula (I)



(I)

in which R is hydrogen or methyl, R^1 is a linear or branched alkyl radical having 1 to 6 carbon atoms, R^2 and R^3 are each independently hydrogen or a group of the formula -COOR' in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms,

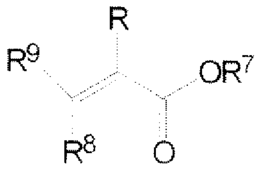
b) 5 to 100% by weight, based on the weight of the monomer composition for preparation of the nonpolar segments, of one or more ethylenically unsaturated ester compounds of the formula (II)



(II)

in which R is hydrogen or methyl, R^4 is a linear or branched alkyl radical having 7 to 15 carbon atoms, R^5 and R^6 are each independently hydrogen or a group of the formula -COOR'' in which R'' is hydrogen or an alkyl group having 7 to 15 carbon atoms,

c) 0 to 80% by weight, based on the weight of the monomer composition for preparation of the nonpolar segments, of one or more ethylenically unsaturated ester compounds of the formula (III)

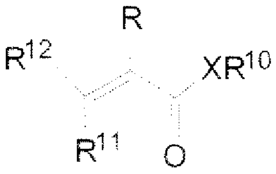


(III)

in which R is hydrogen or methyl, R^7 is a linear or branched alkyl radical having 16 to 30 carbon atoms, R^8 and R^9 are each independently hydrogen or a group of the formula -COOR''' in which R''' is hydrogen or an alkyl group having 16 to 30 carbon atoms,

d) 0 to 50% by weight, based on the weight of the monomer composition for preparation of the hydrophobic segments, of comonomer.

9. A copolymer as claimed in at least one of the preceding claims, characterized in that the dispersing repeat units are derived from one or more ethylenically unsaturated, polar ester compounds of the formula (IV)



(IV)

in which R is hydrogen or methyl, X is oxygen, sulfur or an amino group of the formula -NH- or $-NR^a-$ in which R^a is an alkyl radical having 1 to 40 carbon atoms, R^{10} is a radical which comprises 2 to 1000 carbon atoms and has at least one heteroatom, R^{11} and R^{12} are each independently hydrogen or a group of the formula $-COX'R^{10'}$ in which X' is oxygen or an amino group of the formula -NH- or $-NR^{a'}-$ in which $R^{a'}$ is an alkyl radical having 1 to 40 carbon atoms, and $R^{10'}$ is a radical comprising 1 to 100 carbon atoms, and/or from heterocyclic vinyl compounds.

10. A copolymer as claimed in claim 9, characterized in that the R^{10} radical in at least one of the ester compounds of the formula (IV) comprises at least one group of the formula -CO-.

11. A copolymer as claimed in claim 10, characterized in that the R^{10} radical in at least one of the ester compounds of the formula (IV) comprises at least 2 groups of the formula -CO-.

12. A copolymer as claimed in claim 11, characterized in that the at least two groups of the formula -CO- are bonded to one another via not more than 4 atoms.

13. A copolymer as claimed in at least one of the preceding claims, characterized in that at least one polar segment has dispersing repeat units derived from 2-acetoacetoxyethyl (meth)acrylate.

14. A lubricant comprising at least one copolymer as claimed in at least one of the preceding claims 1 to 13.

15. The lubricant as claimed in claim 14, characterized in that the lubricant comprises at least 10% by weight of group III oil.

16. The use of a copolymer as claimed in at least one of the preceding claims 1 to 13 for improving the coefficient of friction.

17. The use as claimed in claim 16, characterized in that the coefficient of friction is improved in the boundary lubrication range.

18. The use as claimed in claim 16 or 17, characterized in that the HFRR (high frequency reciprocating rig) value is improved.

19. The use of a copolymer as claimed in at least one of the preceding claims 1 to 13 for reducing wear.