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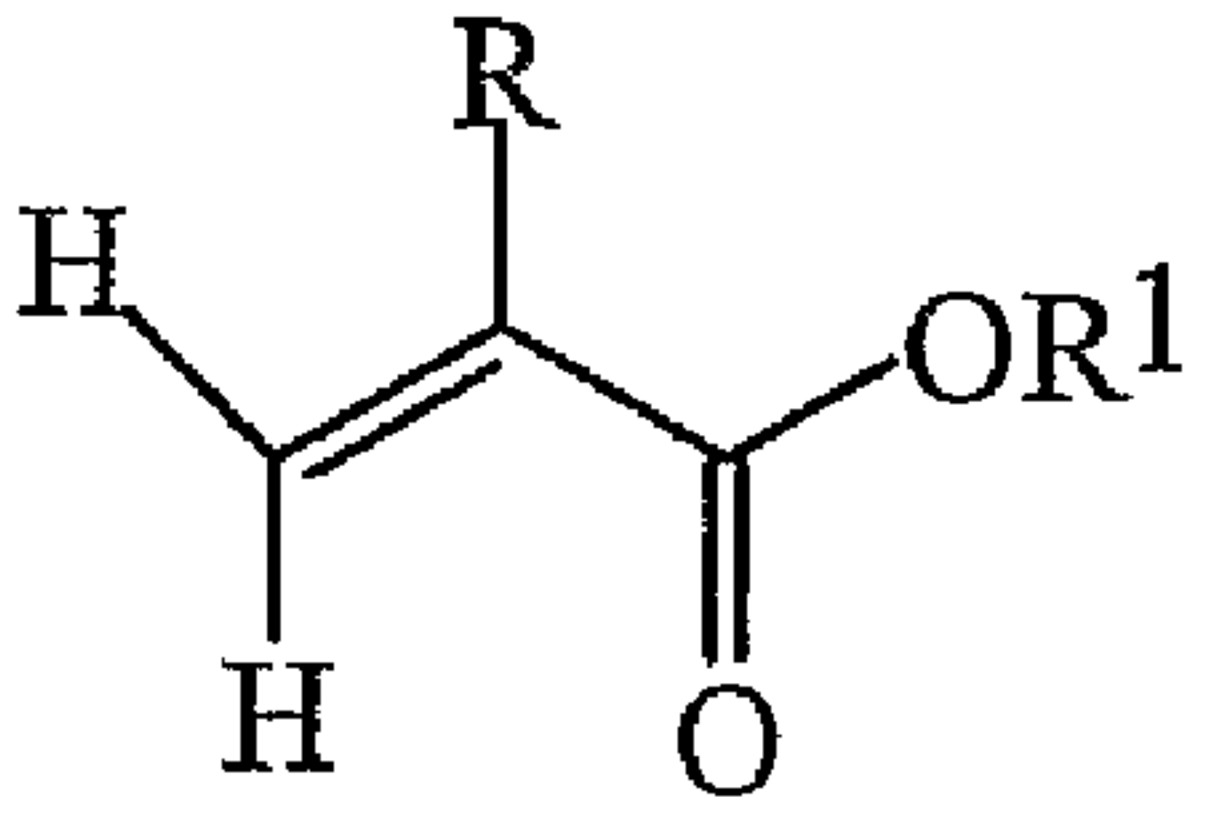
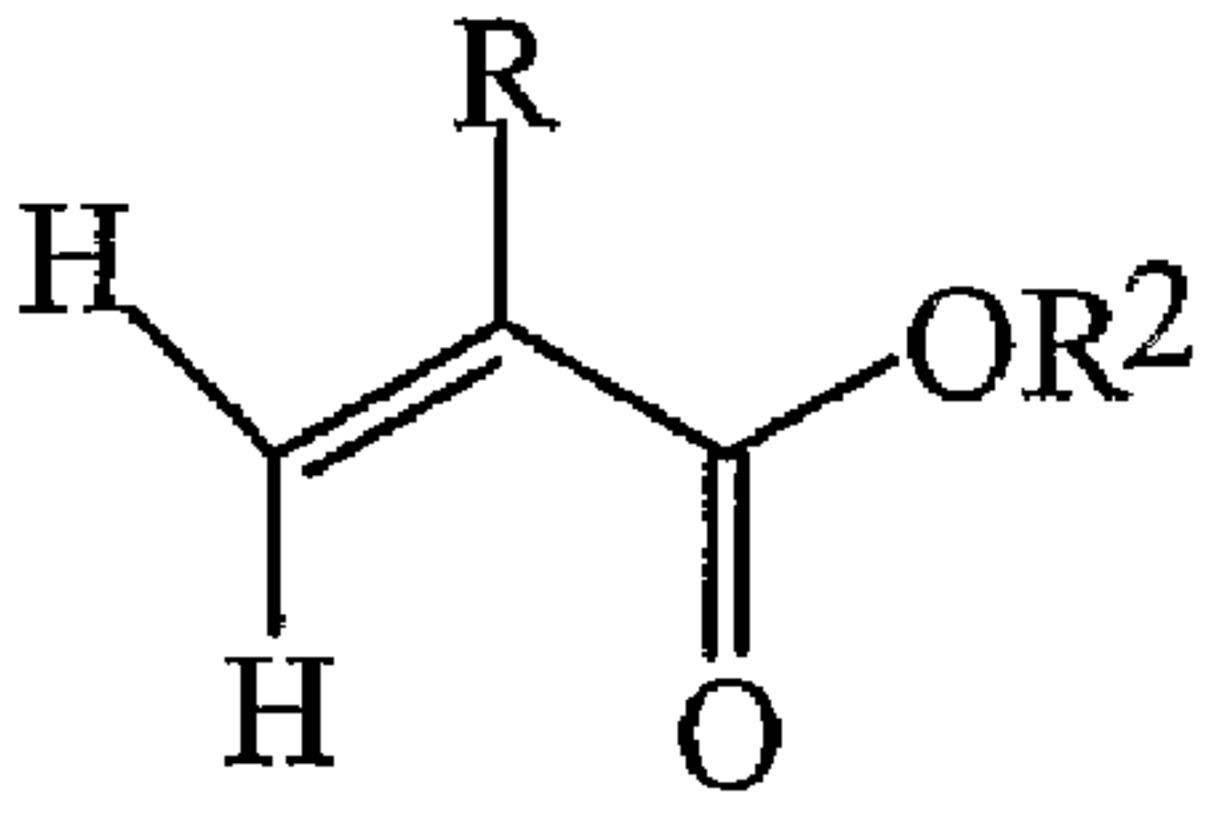
(54) Titre : GRAISSE DE LUBRIFICATION AYANT UNE GRANDE RESISTANCE A L'EAU
(54) Title: LUBRICATING GREASE HAVING A HIGH WATER RESISTANCE


(I)


(II)

(57) Abrégé/Abstract:
The invention relates to lubricating greases containing at least one thickening agent and at least one lubricating oil. The lubricating grease contains at least one polymeric structure improver that can be obtained by polymerizing monomer compositions comprised of: a) 0 to 40 % by weight, with regard to the weight of the monomer compositions for producing the polymer structure improvers, of at least one (meth)acrylate of formula (I), in which R represents hydrogen or methyl, R' represents a linear or branched alkyl radical with 1 to 5 carbon atoms; b) 40 to 99.99 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of at least one (meth) acrylate of formula (II), in which R represents hydrogen or methyl and R^2 represents a linear or branched alkyl radical with 6 to 30 carbon atoms; c) 0.01 to 20 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of acid groups containing monomers or salts thereof, and; d) 0 to 59.99 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of comonomers.

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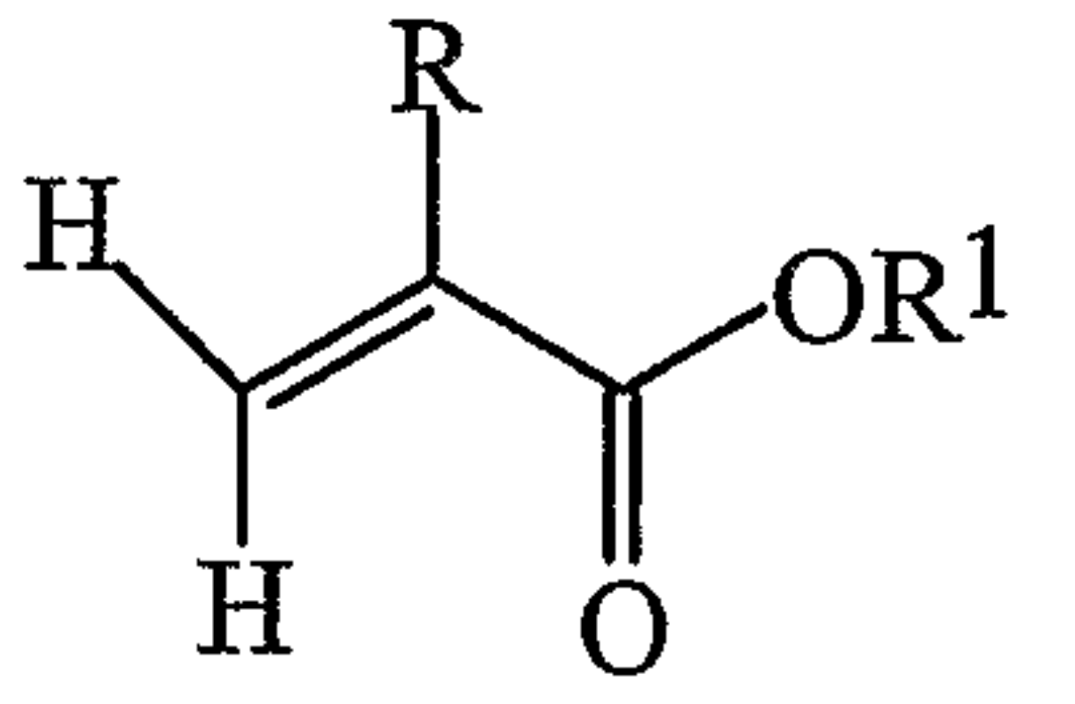
[Fortsetzung auf der nächsten Seite]

(54) Title: LUBRICATING GREASE HAVING A HIGH WATER-RESISTANCE

(54) Bezeichnung: SCHMIERFETT MIT HOHER WASSERRESISTENZ



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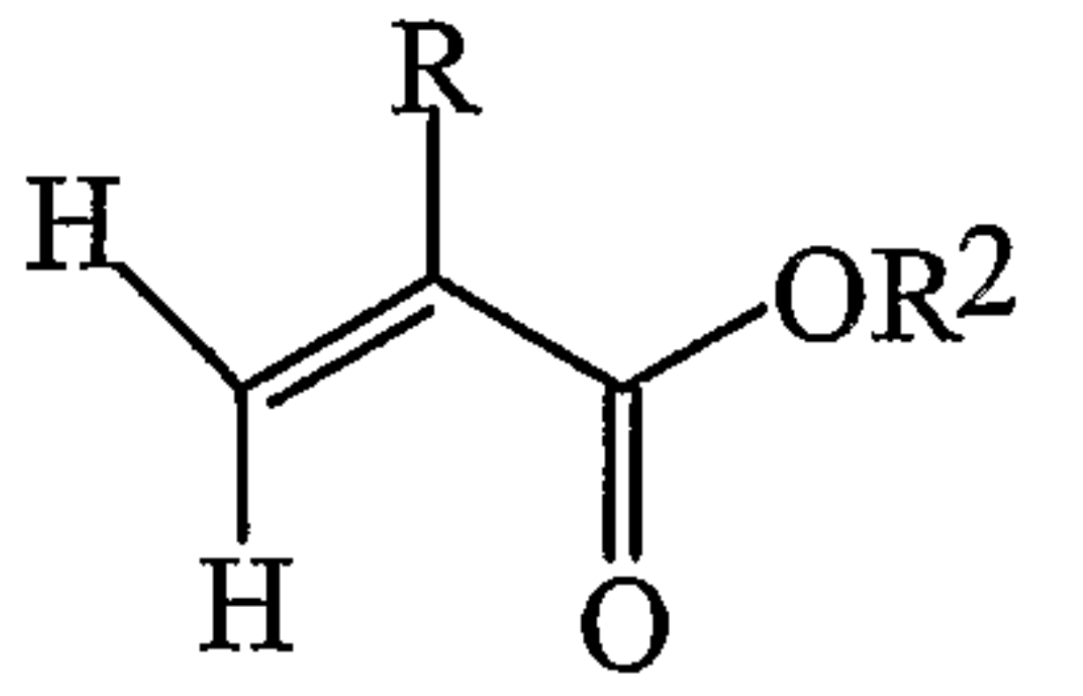

(II)

(57) Abstract: The invention relates to lubricating greases containing at least one thickening agent and at least one lubricating oil. The lubricating grease contains at least one polymeric structure improver that can be obtained by polymerizing monomer compositions comprised of: a) 0 to 40 % by weight, with regard to the weight of the monomer compositions for producing the polymer structure improvers, of at least one (meth)acrylate of formula (I), in which R represents hydrogen or methyl, R' represents a linear or branched alkyl radical with 1 to 5 carbon atoms; b) 40 to 99.99 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of at least one (meth) acrylate of formula (II), in which R represents hydrogen or methyl and R^2 represents a linear or branched alkyl radical with 6 to 30 carbon atoms; c) 0.01 to 20 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of acid groups containing monomers or salts thereof, and; d) 0 to 59.99 % by weight, with regard to the weight of the monomer compositions for producing the polymeric structure improvers, of comonomers.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft Schmierfette umfassend mindestens ein Verdickungsmittel und mindestens ein Schmieröl, wobei das Schmierfett mindestens einen polymeren Strukturverbesserer enthält, der durch Polymerisation von Monomerenzusammensetzungen erhalten werden kann, die aus a) 0 bis 40 Gew.-%, bezogen auf das Gewicht der Monomerenzusammensetzungen zur Herstellung der polymeren Strukturverbesserer, mindestens eines (Meth)acrylats der Formel (I), worin R Wasserstoff oder Methyl darstellt, R' einen linearen oder verzweigten Alkylrest mit 1 bis 5 Kohlenstoffatomen bedeutet, b) 40 bis 99,99 Gew.-%, bezogen auf das Gewicht der Monomerenzusammensetzungen zur Herstellung der polymeren Strukturverbesserer, mindestens eines (Meth)acrylats der Formel (II) worin R Wasserstoff oder Methyl darstellt, R^2 einen linearen oder verzweigten Alkylrest mit 6 bis 30 Kohlenstoffatomen bedeutet, c) 0,01 bis 20 Gew.-%, bezogen auf das Gewicht der Monomerenzusammensetzungen zur Herstellung der polymeren Strukturverbesserer, Säuregruppen umfassende Monomere oder deren Salze, d) 0 bis 59,99 Gew.-%, bezogen auf das Gewicht der Monomerenzusammensetzungen zur Herstellung der polymeren Strukturverbesserer, Comonomer besteht.

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

Lubricating grease having a high water resistance

The present invention relates to lubricating grease having high water resistance.

Lubricating greases are known per se and are used in many ways. Lubricating greases, also referred to hereinafter as "greases", are solid to semifluid substances which are formed by dispersion of a thickener in a fluid lubricant. Other additives which impart particular properties may be present.

The basic consistency of a grease is determined by the combination of base fluid and thickener. The base fluid is generally a base oil customary in the lubricants industry, for example mineral oil, synthetic oil or vegetable oil.

The thickeners used are very frequently, but not exclusively, simple metal soaps. Also used, but less frequently, are complex metal soaps, organically modified clays (bentonite) or polyurea. Viewed in physical terms, the thickeners form the solid phase of the dispersion and, in addition to the base oil, crucially determine the physical/mechanical properties of the grease, for example low-temperature behavior, water resistance, dropping point or oil deposition behavior.
The different combinations of base oil and thickener are known to the expert and determine the field of use of the grease in the industrial application.

In recent times, polymers have increasingly found use in addition to the known thickeners. In addition to an increase in the viscosity of the base oil (thickening effect), they frequently also bring about a change in the structure of the inorganic thickener (structure-modifying action).

The action of polymers as thickeners or viscosity index improvers has already been established for some time in the lubricants industry for base oils, for example mineral oils, synthetic oils or vegetable oils, and is prior art. However, the use of polymers and their action in greases is relatively novel and only demonstrated by a few examples from the literature.

US 3,476,532, Hartman, Nov. 4, 1969, describes metal complexes of oxidized polyethylene containing functional oxygen groups, for example carbonyl, carboxyl or hydroxyl groups. The material can be utilized to produce lubricating grease-like compositions. The composition consists of a mixture of oxidized polyethylene and a complexing agent selected from at least divalent metal salts, fatty acids and metal complexes.

US 3,705,853, Fau et al., Sept. 23, 1970 describes a lubricating grease consisting of a paraffinic mineral oil, a calcium complex soap thickener and an organic terpolymer consisting of 65% ethylene, 5% ester comonomer and 0.01-3% acid-containing comonomer with a melt index between 0.5 and 200. The greases have better water resistance, measured with the water washout test to ASTM D 1264.

US 4,877,557, Kaneshige et al., Oct. 31, 1989 describes a lubricant composition comprising a synthetic lubricant oil, a wear protection additive and a liquid, modified copolymer of ethylene and alpha-olefin having a number-average molecular weight between 300 and 12 000 g/mol.

US 5,116,522, Brown et al., Aug. 23, 1989 describes a lubricant composition consisting of ethylene copolymers, a lubricant oil, a thickener and a viscosity index improver. The ethylene copolymer is a polymer of isobutylene or a copolymer of ethylene, butylene or isobutylene with a C3- to C30-olefin. The viscosity index improvers used are copolymers consisting of 60-90% ethylene and 40-10% vinyl acetate, alkyl acrylates or alkyl methacrylates. The composition has very good high-temperature adhesion and low-temperature softening.

EP 806,469 and US 5,858,934, Wiggins et al., May 8, 1996 describe an improved-biodegradability lubricating grease composition composed of a base oil on a natural basis or based on a synthetic triglyceride, a performance additive consisting of an alkylphenol, a benzotriazole, or composed of an aromatic amine and a thickener which is the reaction product of a metal-based material and a carboxylic acid or ester thereof. In addition, the lubricating grease may likewise comprise viscosity modifiers, pour point improves or the combination of the two.
There is no further discussion on the nature of the viscosity modifier or of the pour point improve.

US 6,300,288, Curtis et al., March 31, 1994 describes a lubricating grease consisting of an oil with a viscosity typical of a lubricant, a polymer which has been modified with an acid functionality and consists of an α-olefin/diene copolymer or a hydrogenated α-olefin/diene copolymer, a metallic species capable of interaction with the acid functionality of the polymer in order to achieve an association between the acid groups, and a co-thickener. The lubricating grease has improved rheological properties. The co-thickener and the metallic species can together form a thickened, overbased material, in the specific case an overbased carboxylate.

Generally, the use of unfunctionalized, purely polyolefinic polymers has been described sufficiently in the literature, for example in Tribol. Schmierungstech. (1995), 42(2), 92-96 for polyisobutylenes and in J. Synth. Lubric. 4 (1987) for linear, branched and partly branched polyethylenes; isotactic polypropylenes, poly-1-butenes and poly(4-methyl-1-pentenes).

The use of reactively changed copolymers based on olefin copolymers (OCPs) has to date remained restricted to a few examples and is described, inter alia, in NLGI Spokesman, Vol. 59, No. 10, Feb. 1999.

The use of polyalkylene acrylates and polyalkyl methacrylates (PAMAs) as viscosity index improvers and pour point improves is known in the literature and industry (Wilfried J. Bartz et al., Schmierfette, expert-Verl., 2000, ISBN 3-8169-1533-7, Wilfried J. Bartz et al., Additive für Schmierstoffe, expert-Verl., 1994, ISBN 3-8169-0916-7).

According to the prior art detailed above, the addition of polymers to lubricating greases improves certain physical parameters, for example rheological properties or the water resistance of the greases. On the other hand, it should be emphasized that there is a permanent need to further improve these properties. In particular, the aim is to achieve a better property profile. At the same time, the improvement in one property, for example the water resistance, should not be associated with an excessively great deterioration in other properties, for example in the handling or the homogeneity.
In particular, the lubricating greases should have a particularly high water resistance, an excellent consistency and a high homogeneity.

A further object can be considered to be that of providing lubricating greases with improved thermal properties. In particular, the properties at low temperatures should be improved. Moreover, the lubricating greases should be usable over a particularly wide temperature range.

It was therefore an object of the present invention to provide a lubricating grease with particularly high homogeneity.

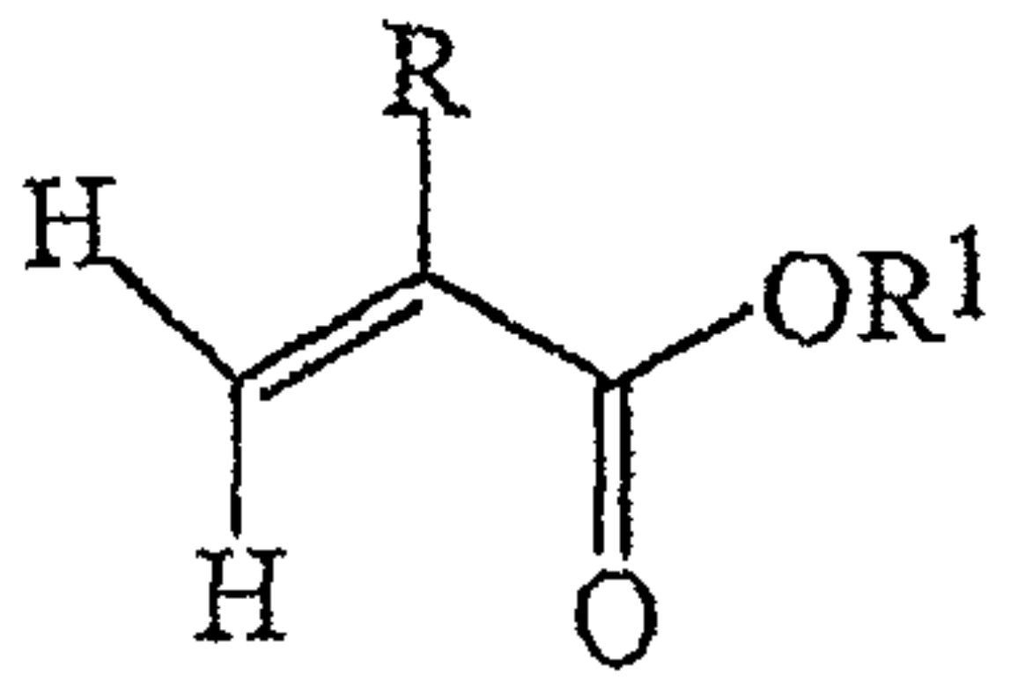
Moreover, the lubricating greases should be producible inexpensively. At the same time, they should be producible on the industrial scale without new plants or plants with complicated construction being required for this purpose.

These objects and further objects which are not stated explicitly but which can be derived or discerned from the connections discussed by way of introduction herein are achieved by lubricating greases as described below.

In one embodiment, a lubricating grease of the present invention comprises:

A lubricating grease comprising at least one thickening agent, at least one lubricating oil, and at least one polymeric structure improver obtained by polymerization of monomer compositions, which comprise:

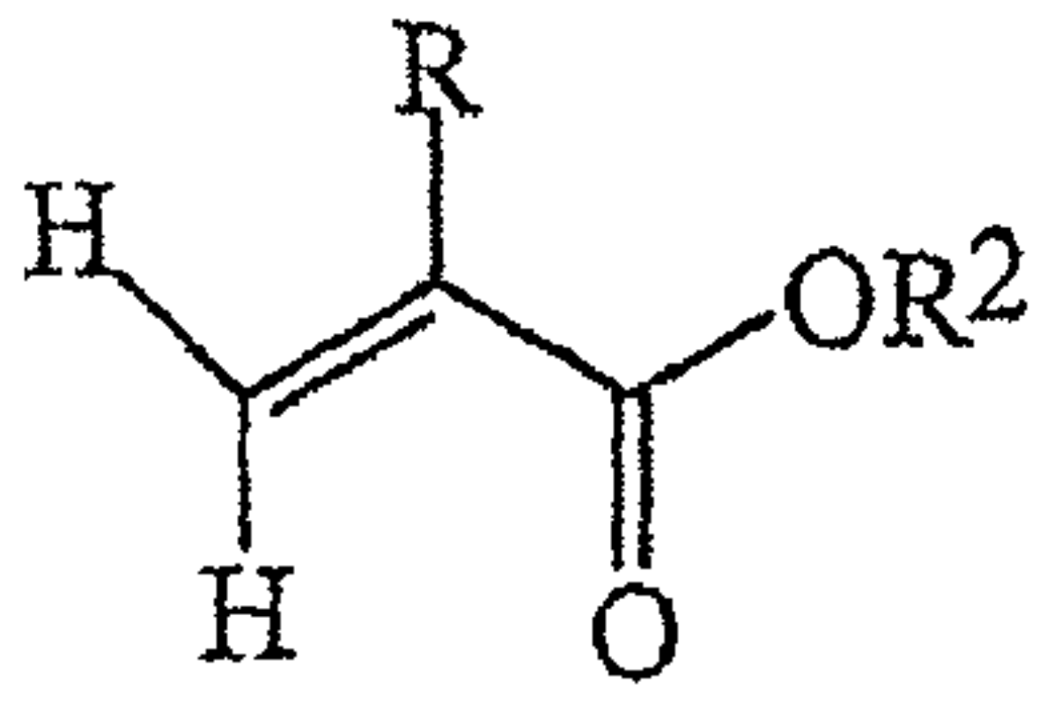
a) optionally, 0 to 40 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of at least one (meth)acrylate of formula (I)



(I),

in which R represents hydrogen or methyl, R^1 denotes a straight-chain or branched alkyl moiety having 1 to 5 carbon atoms,

b) 40 to 99.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of at least one (meth)acrylate of formula (II)



(II),

in which R represents hydrogen or methyl, R^2 denotes a straight-chain or branched alkyl moiety having 6 to 30 carbon atoms,

c) 0.01 to 5 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of monomers containing acid groups or salts thereof,

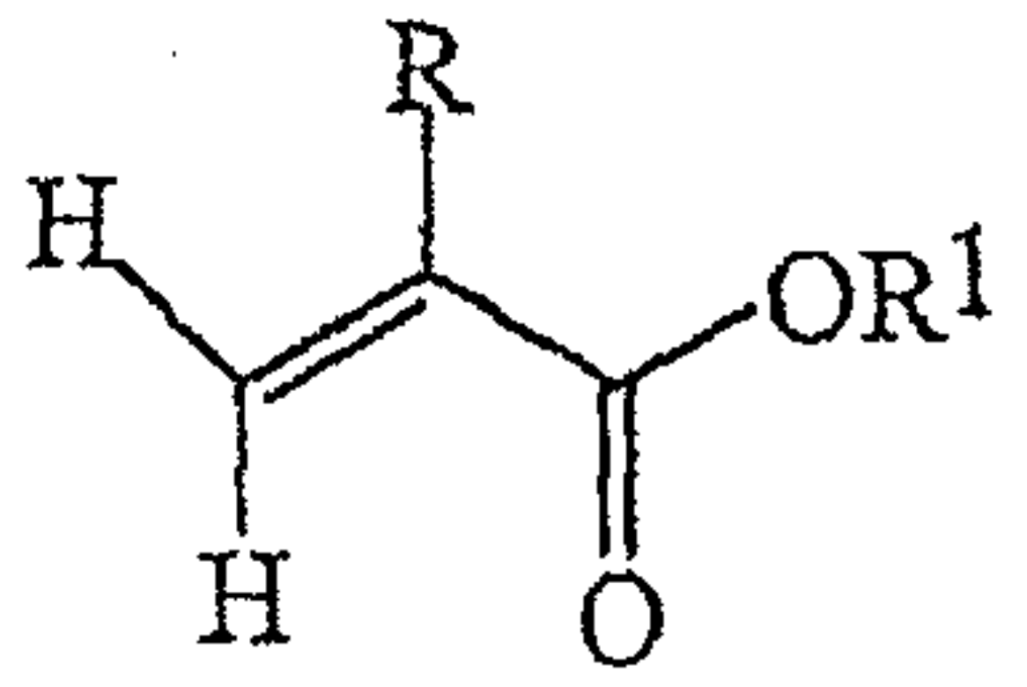
d) optionally, 0 to 59.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of comonomer.

In one embodiment, at least part of the monomers according to component c) contains at least one carboxyl group, at least one phosphonic acid group, at least one sulfonic acid group or a combination thereof.

In a further embodiment, component c) contains at least one monomer selected from the group comprising methacrylic acid, acrylic acid, a combination thereof or salts thereof.

In another embodiment, the present invention provides a method for production of lubricating grease, comprising producing a mixture comprising at least one thickening agent, at least one lubricating oil and a polymeric structure improver, which is obtained by polymerization of monomer compositions, which comprise

a) optionally, 0 to 40 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of one or more ethylenically unsaturated ester compounds of formula (I)



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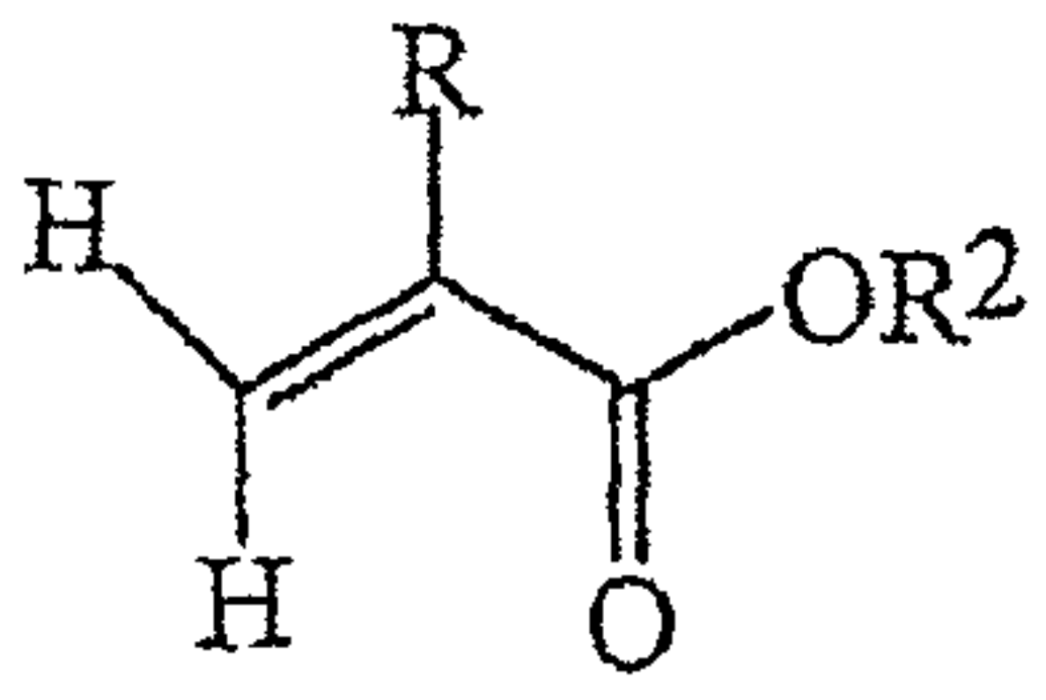
in which R represents hydrogen or methyl, R^1 denotes a straight-chain or branched alkyl moiety having 1 to 5 carbon atoms,

b) 40 to 99.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of one or more ethylenically unsaturated ester compounds of formula (II)



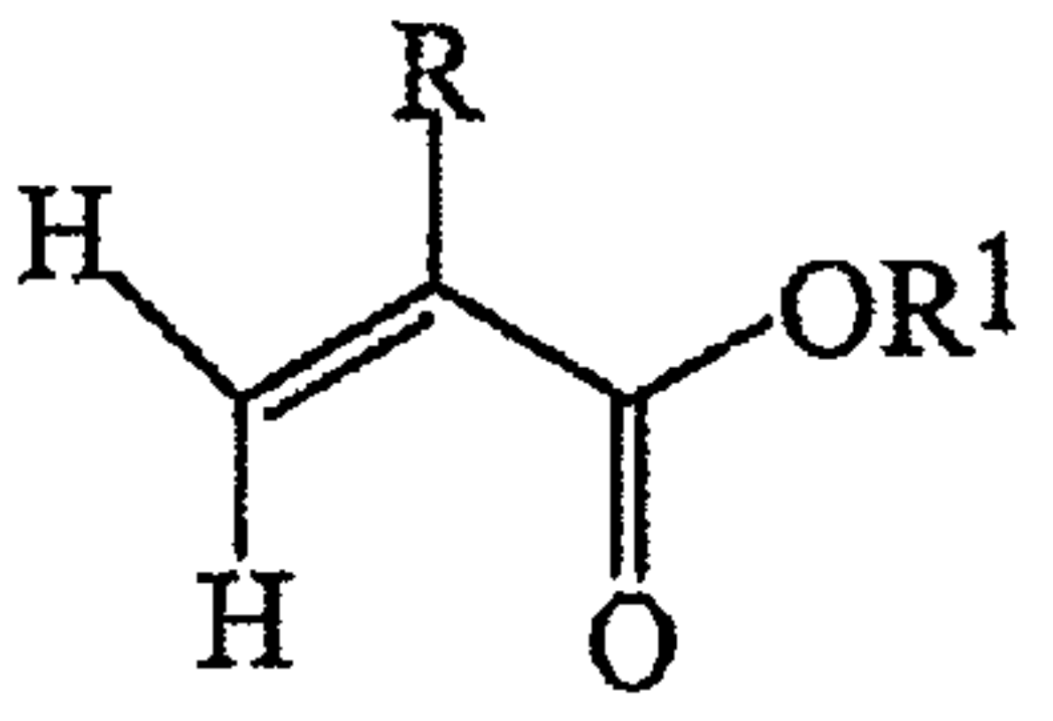
(II),

in which R represents hydrogen or methyl, R^2 denotes a straight-chain or branched alkyl moiety having 6 to 30 carbon atoms,

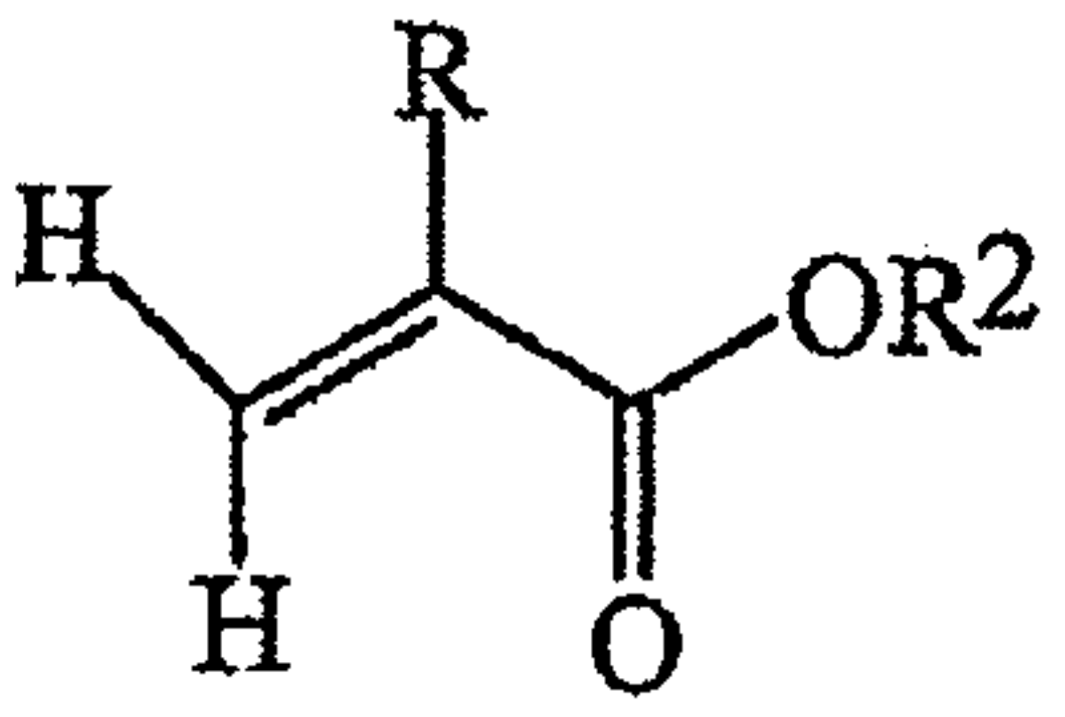
c) 0.01 to 20 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of monomers containing acid groups or salts thereof,

d) optionally, 0 to 59.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of comonomer.

By virtue of a lubricating grease which comprises at least one thickener and at least lubricant oil comprising a polymeric structure improver which can be obtained by polymerizing monomer compositions which consist of
a) from 0 to 40% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of at least one (meth)acrylate of the formula (I)


(I),

where R is hydrogen or methyl, R^1 is a linear or branched alkyl radical having from 1 to 5 carbon atoms,
b) from 40 to 99.99% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of at least one (meth)acrylate of the formula (II)


(II),

where R is hydrogen or methyl, R^2 is a linear or branched alkyl radical having from 6 to 30 carbon atoms,
c) from 0.01 to 20% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of monomers comprising acid groups or salts thereof,
d) from 0 to 59.99% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of comonomer,
it is possible in a not directly foreseeable manner to provide lubricating greases which have improved properties.

At the same time, the inventive lubricating greases can achieve a series of further advantages. These include:

- The inventive lubricating greases have very high water resistance.

- The inventive lubricating greases exhibit good homogeneity. The consistency of the lubricating grease is adjustable within a wide range.

- The inventive lubricating greases have very good thermal properties. Thus, the inventive lubricating greases can be used over a particularly wide temperature range. In addition, the properties at low temperatures are outstanding.

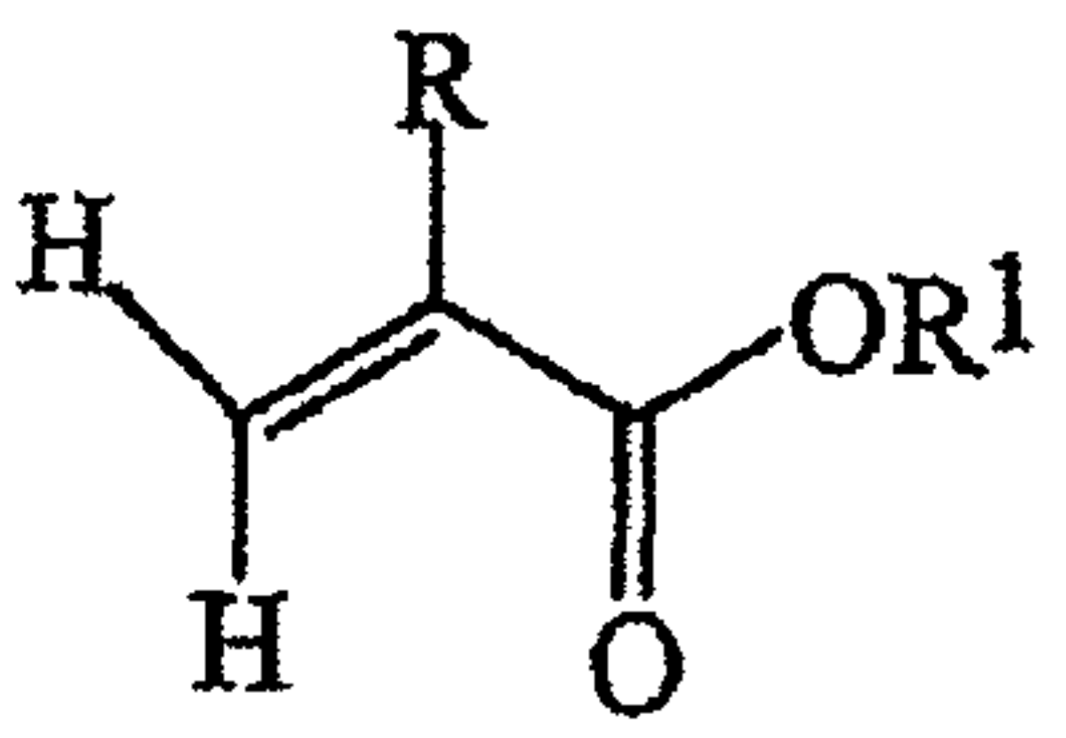
- Furthermore, the inventive lubricating greases can be produced subsequently by modification of known lubricating greases, in which case a polymeric structure improver is added to a known grease. In particular, this allows high storage costs to be avoided. Furthermore, it is possible to react rapidly to the wishes of customers. This changes the consistency of the lubricating grease only slightly, whereas the water resistance increases greatly.

- The lubricating greases of the present invention can be produced in a particularly easy and simple manner. It is possible to use customary, industrial-scale plants.

- Furthermore, it is possible in particular to use commercially available components in the processes for producing the lubricating greases.

The inventive lubricating greases comprise polymeric structure improvers. These polymers lead generally to an improvement in the water resistance. It is assumed in this context that these polymers enter into physico-chemical interaction with the thickeners, for example the soap molecules, without any intention that this should impose a restriction.

Mixtures from which the polymeric structure improvers are obtainable may contain from 0 to 40% by weight, in particular from 0.5 to 20% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of at least one (meth)-acrylate of the formula (I)

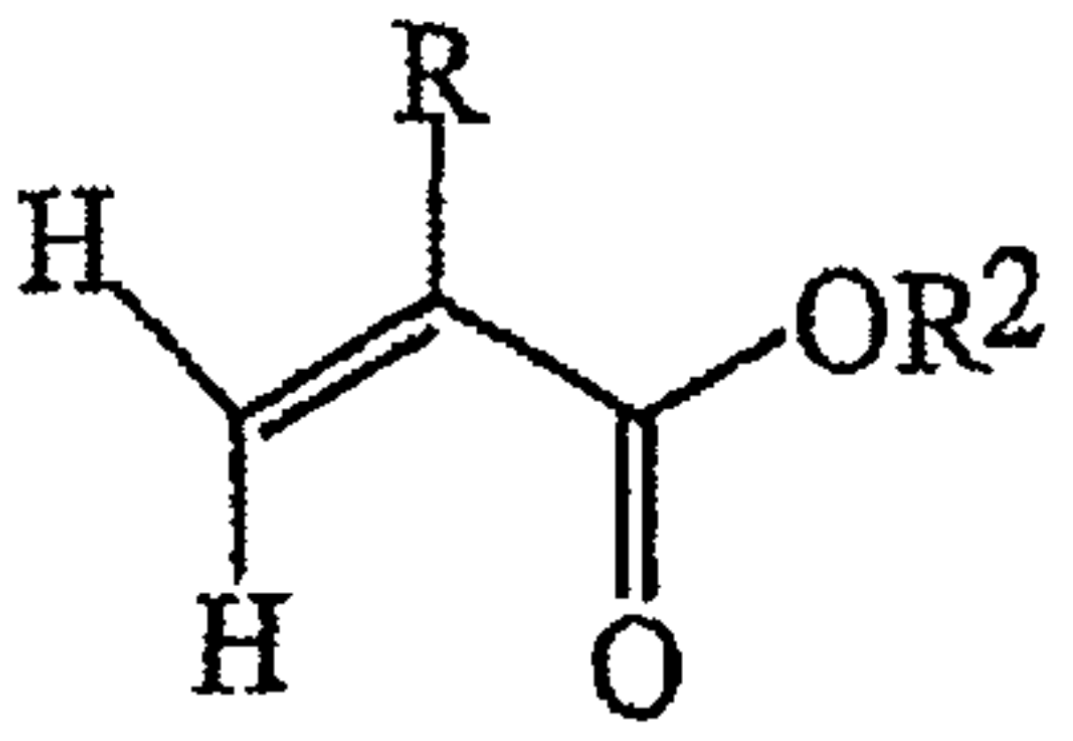


(I),

where R is hydrogen or methyl, R^1 is a linear or branched alkyl radical having from 1 to 5 carbon atoms. The term (meth)acrylates encompasses methacrylates and acrylates, and also mixtures of the two. These monomers are widely known. The alkyl radical may be linear, cyclic or branched.

Examples of component a) include
(meth)acrylates which derive from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate and pentyl (meth)acrylate;
cycloalkyl (meth)acrylates such as cyclopentyl (meth)acrylate;
(meth)acrylates which derive from unsaturated alcohols, such as 2-propynyl (meth)acrylate, allyl (meth)acrylate and vinyl (meth)acrylate.

As a further constituent, the compositions to be polymerized to prepare preferred polymeric structure improvers contain from 40 to 99.99% by weight, in particular from 55 to 95% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of at least one (meth)acrylate of the formula (II)



(II),

where R is hydrogen or methyl, R^2 is a linear or branched alkyl radical having from 6 to 30 carbon atoms.

These include:

(meth)acrylates which derive from saturated alcohols, such as hexyl (meth)acrylate, 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, 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;

(meth)acrylates which derive from unsaturated alcohols,

for example oleyl (meth)acrylate;
cycloalkyl (meth)acrylates such as 3-vinylcyclohexyl (meth)acrylate, cyclohexyl (meth)acrylate, bornyl (meth)acrylate.

The (meth)acrylates with a long-chain alcohol radical, in particular the compounds as per component (b), can be obtained, for example, by reacting (meth)acrylates and/or the corresponding acids with long-chain fatty alcohols, which generally forms a mixture of esters, for example (meth)acrylates with various long-chain alcohol radicals. These fatty alcohols include Oxo Alcohol® 7911 and Oxo Alcohol® 7900, Oxo Alcohol® 1100 from Monsanto; Alphanol® 79 from ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 from Sasol; Epal® 610 and Epal® 810 from Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25L from Shell AG; Lial 125™ from Sasol; Dehydad® and Lorol® types from Cognis.

In a particular aspect of the present invention, the mixture for preparing preferred polymeric structure improvers has at least 60% by weight, preferably at least 70% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers, of monomers of the formula (II).

In general, the methacrylates are preferred over the acrylates.

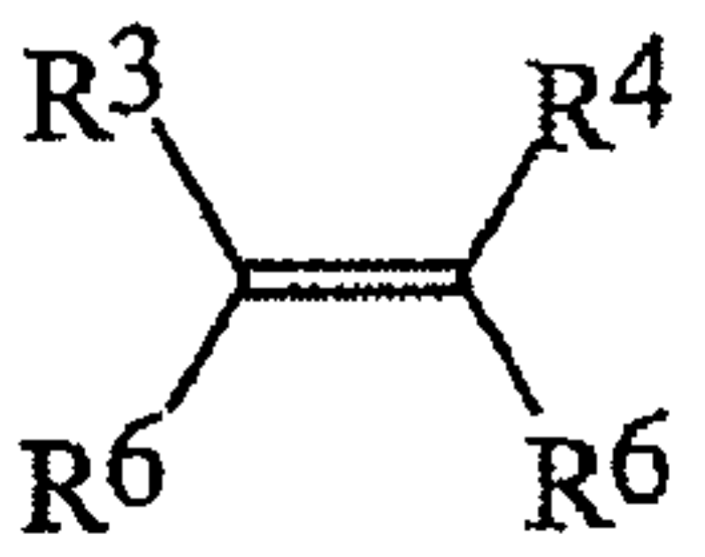
In a particular aspect of the present invention, preference is given to using mixtures of long-chain alkyl (meth)acrylates as per component b), the mixtures comprising at least one (meth)acrylate having from 6 to 15 carbon atoms in the alcohol radical and at least one (meth)acrylate having from 16 to 30 carbon atoms in the alcohol radical. The proportion of the (meth)acrylates having from 6 to 15 carbon atoms in the alcohol radical is preferably in the range from 20 to 95% by weight, based on the weight of the monomer composition for preparing the polymeric structure improvers. The proportion of the (meth)acrylates having from 16 to 30 carbon atoms in the alcohol radical is preferably in the range from 0.5 to 60% by weight, based on the weight of the monomer composition for preparing the polymeric structure improvers.

Component c) of the composition to be used to prepare preferred polymeric structure improvers comprises in particular monomers comprising acid groups or salts thereof.

Preferred salts are in particular the alkali metal salts, for example the lithium, sodium and/or potassium salts; the alkaline earth metal salts, for example the calcium and/or barium salts, and the aluminum salts and the ammonium salts.

The proportion of components c) is generally from 0.01 to 20% by weight, preferably from 0.1 to 10% by weight and more preferably from 0.5 to 5% by weight, based on the weight of the monomer compositions for preparing the polymeric structure improvers.

Monomers comprising acid groups are known in the technical field. These can be represented in many cases by the formula (III)



(III),

where R^3 and R^4 are each independently selected from the group consisting of hydrogen, halogens, CN, linear or branched alkyl groups having from 1 to 20, preferably from 1 to 6 and more preferably from 1 to 4 carbon atoms, which may be substituted by from 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 from 2 to 10, preferably from 2 to 6 and more preferably from 2 to 4 carbon atoms, which may be substituted by from 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 from 3 to 8 carbon atoms which may be substituted by from 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the cycloalkyl group; aryl groups having from 6 to 24 carbon atoms which may be substituted by from 1 to (2n-1) halogen atoms, preferably chlorine, and/or alkyl groups having from 1 to 6 carbon atoms, where n is the number of carbon atoms of the aryl group; $COOR^7$, $-SO_3R^7$ and/or $PO_3R^7{}_2$ where R^7 is independently hydrogen, an alkali metal, an alkaline earth metal and/or aluminum, an ammonium group having up to 20 carbon atoms or an alkyl group having from 1 to 40 carbon atoms;

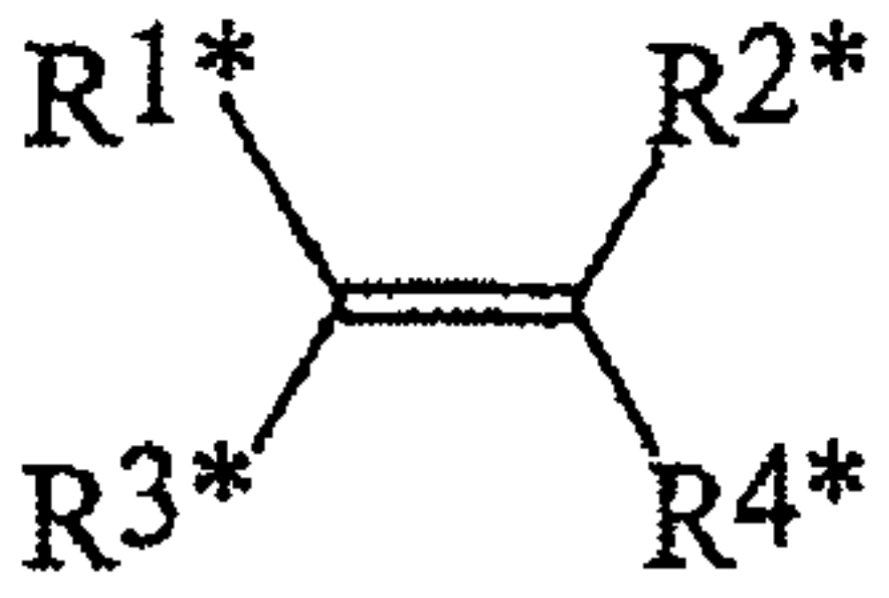
R^5 and R^6 are each independently selected from the group consisting of hydrogen, halogen (preferably fluorine or chlorine), alkyl groups having from 1 to 6 carbon atoms and $COOR^7$, $-SO_3R^7$ and/or $PO_3R^7{}_2$ where R^7 is independently hydrogen, an alkali metal, an ammonium group having up to 20 carbon atoms or an alkyl group having from 1 to 40 carbon atoms, where R^7 is hydrogen, an alkali metal, an alkaline earth metal and/or aluminum or an alkyl group having from 1 to 40 carbon atoms, or R^5 and R^6 may together form a group of the formula $(CH_2)_{n'}$ which may be substituted by from 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 from 2 to 6, preferably 3 or 4, and Y may be NR^8, S or O, preferably O, where R^8 is hydrogen, linear or branched alkyl or aryl groups having from 1 to 20 carbon atoms; where at least two of the R^3, R^4, R^5

and R^6 radicals are each hydrogen or halogen and at least one of the R^3, R^4, R^5 and R^6 radicals comprises at least one group of the formula -COOM, $-SO_3M$ and/or PO_3M_2, where M is independently hydrogen, an alkali metal, an alkaline earth metal and/or aluminum.

These compounds can generally be copolymerized with the monomers as per component a), b) and d). They include ethylenically unsaturated compounds, for example vinylsulfonic acid, vinylphosphonic acid, acrylic acid, methacrylic acid, fumaric acid, monoesters of fumaric acid, where the alcohol radical may comprises generally from 1 to 30 carbon atoms, maleic acid, monoesters of maleic acid, where the alcohol radical may generally comprise from 1 to 30 carbon atoms, vinylbenzoic acid and sulfonated styrenes such as styrenesulfonic acid. In addition, the salts derived from these acids, in particular the alkali metal, alkaline earth metal and/or aluminum salts, may be used.

Component d) of the composition to be used to prepare preferred polymeric structure improvers comprises in particular ethylenically unsaturated monomers which can be copolymerized with the monomers as per components a) to c).

However, particularly suitable comonomers for polymerization according to the present invention are those which correspond to the formula:



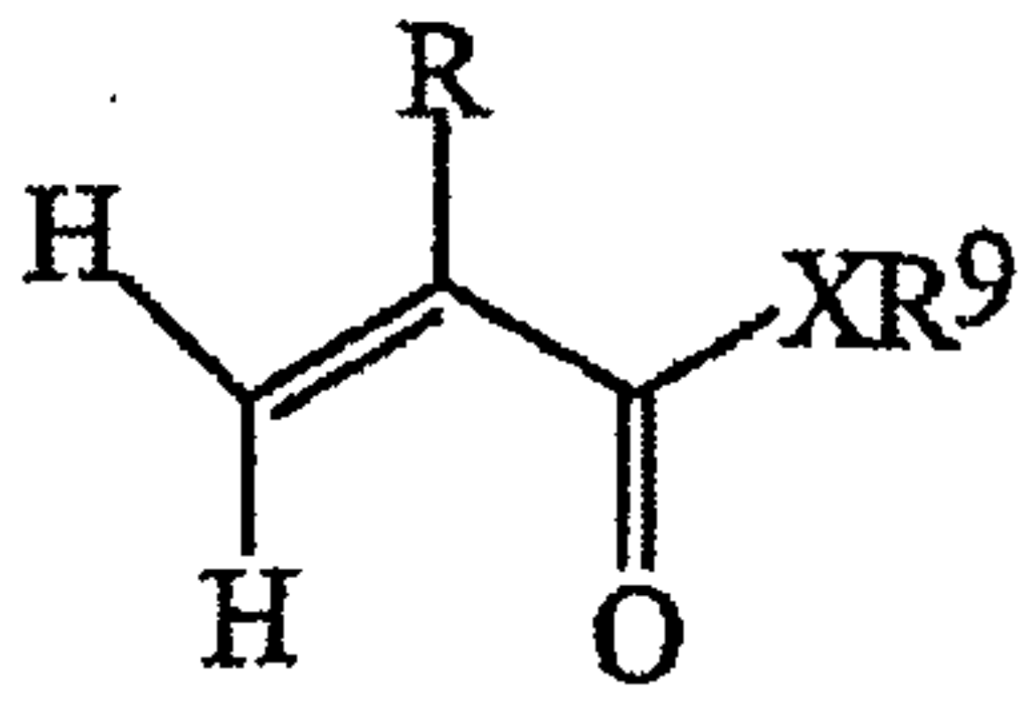
in which R^{1*} and R^{2*} are each independently selected from the group consisting of hydrogen, halogens, CN, linear or branched alkyl groups having from 1 to 20, preferably from 1 to 6 and more preferably from 1 to 4, carbon atoms which may be substituted by from 1 to (2n+1) halogen atoms, where n 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 from 2 to 10, preferably from 2 to 6 and more preferably from 2 to 4, carbon atoms which may be substituted by from 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 from 3 to 8 carbon atoms which may be substituted by from 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the cycloalkyl group; aryl groups having from 6 to 24 carbon atoms which may be substituted by from 1 to (2n-1) halogen atoms, preferably chlorine and/or alkyl groups having from 1 to 6 carbon atoms, where n is the number of carbon atoms of the aryl group; $COOR^{9*}$ where R^{9*} is an alkyl group having from 1 to 40 carbon atoms; $C(=Y^*)R^{5*}$, $C(=Y^*)NR^{6*}R^{7*}$, $Y^*C(=Y^*)R^{5*}$, 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 from 1 to 20 carbon atoms, an alkylthio having from 1 to 20 carbon atoms, OR^{10*} (R^{10*} is hydrogen or an alkali metal), alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^{6*} and R^{7*} are each independently hydrogen or an alkyl group having from 1 to 20 carbon atoms, or R^{6*} and R^{7*} together may form an alkylene group having from 2 to 7, preferably from 2 to 5 carbon atoms, in which case they form a 3- to 8-membered, preferably 3- to 6-membered, ring, and R^{8*} is hydrogen, linear or branched alkyl or aryl groups having from 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 from 1 to 6 carbon atoms and $COOR^{9*}$ in which R^{9*} is an alkyl group having from 1 to 40 carbon atoms, or R^{3*} and R^{4*} together may form a group of the formula $(CH_2)_{n'}$ which may be substituted by from 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 from 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.

These include:
aryl (meth)acrylates such as benzyl methacrylate or phenyl methacrylate in which the aryl radicals may each be unsubstituted or up to tetrasubstituted;
methacrylates of halogenated alcohols, such as
2,3-dibromopropyl methacrylate,
4-bromophenyl methacrylate,
1,3-dichloro-2-propyl methacrylate,
2-bromoethyl methacrylate,
2-iodoethyl methacrylate,
chloromethyl methacrylate;
vinyl halides, for example vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;
vinyl esters such as vinyl acetate;
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;
heterocyclic vinyl compounds such as 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, 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;
vinyl and isoprenyl ethers;
maleic acid derivatives, for example diesters of maleic acid, where the alcohol radical may generally comprise from 1 to 30 carbon atoms, maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide;
fumaric acid derivatives, for example the diesters of fumaric acid, where the alcohol radical may generally comprise from 1 to 30 carbon atoms;
dienes, for example divinylbenzene.

More preferably, the compositions for preparing preferred structure improvers comprise comonomers as per component d), which can be represented by the formula (IV)



(IV),

where R is independently hydrogen or methyl, R^9 is independently a group which comprises from 2 to 1000 carbon atoms and has at least one heteroatom, X is independently a sulfur or oxygen atom or a group of the formula NR^{10} where R^{10} is independently hydrogen or a group having from 1 to 20 carbon atoms, and n is an integer greater than or equal to 3.

The R^9 radical is a group comprising from 2 to 1000, in particular from 2 to 100, preferably from 2 to 20 carbon atoms. The term "group having from 2 to 1000 carbon" denotes radicals of organic compounds having from 2 to 1000 carbon atoms. It encompasses aromatic and heteroaromatic groups, and also 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 from 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, ether groups, ester groups and halides.

According to the invention, aromatic groups denote radicals of mono- or polycyclic aromatic compounds having preferably from 6 to 20, in particular from 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 from 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, diphenylsulfone, 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, benzooxathiadiazole, benzooxadiazole, 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 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 alkenyl groups include the vinyl, allyl, 2-methyl-2-propenyl, 2-butenyl, 2-pentenyl, 2-decenyl and the 2-eicosenyl group.

The preferred alkynyl groups include the ethynyl, propargyl, 2-methyl-2-propynyl, 2-butynyl, 2-pentynyl and the 2-decynyl group.

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

The preferred alkoxycarbonyl groups include the methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, tert-butoxycarbonyl, 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.

In a particular embodiment of the present invention, the R^8 radical in formula (IV) has at least one group of the formula -OH or $-NR^{10}R^{10}$, in which R^{10} independently includes hydrogen or a group having from 1 to 20 carbon atoms.

The X group in formula (IV) can preferably be represented by the formula NH.

The numerical ratio of heteroatoms to carbon atoms in the R^9 radical of the formula (IV) may lie within wide ranges. This ratio is preferably in the range from 1:1 to 1:10, in particular from 1:1 to 1:5 and more preferably from 1:2 to 1:4.

The R^9 radical of the formula (IV) comprises from 2 to 1000 carbon atoms. In a particular aspect, the R^9 radical has at most 10 carbon atoms.

The preferred comonomers include
hydroxyalkyl (meth)acrylates such as
3-hydroxypropyl methacrylate,
3,4-dihydroxybutyl methacrylate,
2-hydroxyethyl methacrylate,
2-hydroxypropyl methacrylate,
2,5-dimethyl-1,6-hexanediol (meth)acrylate,
1,10-decanediol (meth)acrylate,
carbonyl-containing methacrylates such as
2-carboxyethyl methacrylate,
carboxymethyl methacrylate,
oxazolidinylethyl methacrylate,
N-(methacryloyloxy)formamide,
acetonyl methacrylate,
N-methacryloylmorpholine,
N-methacryloyl-2-pyrrolidinone,
N-(2-methacryloyloxyethyl)-2-pyrrolidinone,
N-(3-methacryloyloxypropyl)-2-pyrrolidinone,
N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone,
N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone;
glycol dimethacrylates such as 1,4-butanediol methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate,
2-ethoxyethyl methacrylate;
methacrylates of ether alcohols, such as
tetrahydrofurfuryl methacrylate,
vinyloxyethoxyethyl methacrylate,
methoxyethoxyethyl methacrylate,
1-butoxypropyl methacrylate,
1-methyl-(2-vinyloxy)ethyl methacrylate,
cyclohexyloxymethyl methacrylate,
methoxymethoxyethyl methacrylate,
benzyloxymethyl methacrylate,
furfuryl methacrylate,
2-butoxyethyl methacrylate,
2-ethoxyethoxymethyl methacrylate,
2-ethoxyethyl methacrylate,

allyloxymethyl methacrylate,
1-ethoxybutyl methacrylate,
methoxymethyl methacrylate,
1-ethoxyethyl methacrylate,
ethoxymethyl methacrylate and ethoxylated (meth)acrylates which have preferably from 1 to 20, in particular from 2 to 8, ethoxy groups;
aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylatamides, such as N-(3-dimethylaminopropyl)methacrylamide,
dimethylaminopropyl methacrylate,
3-diethylaminopentyl methacrylate,
3-dibutylaminohexadecyl (meth)acrylate;
nitriles of (meth)acrylic acid and other nitrogen-containing methacrylates, such as
N-(methacryloyloxyethyl)diisobutyl ketimine,
N-(methacryloyloxyethyl)dihexadecyl ketimine,
methacryloylamidoacetonitrile,
2-methacryloyloxyethylmethylcyanamide,
cyanomethyl methacrylate;
heterocyclic (meth)acrylates such as 2-(1-imidazolyl)ethyl (meth)acrylate, 2-(4-morpholinyl)ethyl (meth)acrylate and 1-(2-methacryloyloxyethyl)-2-pyrrolidone;
oxiranyl methacrylates such as
2,3-epoxybutyl methacrylate,
3,4-epoxybutyl methacrylate,
10,11-epoxyundecyl methacrylate,
2,3-epoxycyclohexyl methacrylate,
10,11-epoxyhexadecyl methacrylate;
glycidyl methacrylate;
sulfur-containing methacrylates such as
ethylsulfinylethyl methacrylate,
4-thiocyanatobutyl methacrylate,
ethylsulfonylethyl methacrylate,
thiocyanatomethyl methacrylate,
methylsulfinylmethyl methacrylate,
bis(methacryloyloxyethyl) sulfide;
phosphorus-, boron- and/or silicon-containing meth-

acrylates such as
2-(dimethylphosphato)propyl methacrylate,
2-(ethylenephosphito)propyl methacrylate,
dimethylphosphinomethyl methacrylate,
dimethylphosphonoethyl methacrylate,
diethylmethacryloyl phosphonate,
dipropylmethacryloyl phosphate, 2-(dibutylphosphono)-ethyl methacrylate,
2,3-butylenemethacryloylethyl borate,
methyldiethoxymethacryloylethoxysilane,
diethylphosphatoethyl methacrylate.
These monomers may be used individually or as a mixture.

The ethoxylated (meth)acrylates can be obtained, for example, by transesterification of alkyl (meth)-acrylates with ethoxylated alcohols which more preferably have from 1 to 20, in particular from 2 to 8 ethoxy groups. The hydrophobic radical of the ethoxylated alcohols may preferably comprise from 1 to 40, in particular from 4 to 22 carbon atoms, and either linear or branched alcohol radicals may be used. In a further preferred embodiment, the ethoxylated (meth)acrylates have an OH end group.

Examples of commercially available ethoxylates which can be employed for the preparation of ethoxylated (meth)acrylates are ethers of the Lutensol® A brands, in particular Lutensol® A 3 N, Lutensol® A 4 N, Lutensol® A 7 N and Lutensol® A 8 N, ethers of the Lutensol® TO brands, in particular Lutensol® TO 2, Lutensol® TO 3, Lutensol® TO 5, Lutensol® TO 6, Lutensol® TO 65, Lutensol® TO 69, Lutensol® TO 7, Lutensol® TO 79, Lutensol® 8 and Lutensol® 89, ethers of the Lutensol® AO brands, in particular Lutensol® AO 3, Lutensol® AO 4, Lutensol® AO 5, Lutensol® AO 6, Lutensol® AO 7, Lutensol® AO 79, Lutensol® AO 8 and Lutensol® AO 89, ethers of the Lutensol® ON brands, in particular Lutensol® ON 30, Lutensol® ON 50, Lutensol® ON 60, Lutensol® ON 65, Lutensol® ON 66, Lutensol® ON 70, Lutensol® ON 79 and Lutensol® ON 80, ethers of the Lutensol® XL brands, in particular Lutensol® XL 300, Lutensol® XL 400, Lutensol® XL 500, Lutensol® XL 600, Lutensol® XL 700, Lutensol® XL 800, Lutensol® XL 900 and Lutensol® XL 1000, ethers of the Lutensol® AP brands, in particular Lutensol® AP 6, Lutensol® AP 7, Lutensol® AP 8, Lutensol® AP 9, Lutensol® AP 10, Lutensol® AP 14 and Lutensol® AP 20, ethers of the IMBENTIN® brands, in particular of the IMBENTIN® AG brands, of the IMBENTIN® U brands, of the IMBENTIN® C brands, of the IMBENTIN® T brands, of the IMBENTIN® OA brands, of the IMBENTIN® POA brands, of the IMBENTIN® N brands and of the IMBENTIN® O brands and ethers of the Marlipal® brands, in particular Marlipal® 1/7, Marlipal® 1012/6, Marlipal® 1618/1, Marlipal® 24/20, Marlipal® 24/30, Marlipal® 24/40, Marlipal® O13/20, Marlipal® O13/30, Marlipal® O13/40, Marlipal® O25/30, Marlipal® O25/70, Marlipal® O45/30, Marlipal® O45/40, Marlipal® O45/50, Marlipal® O45/70 and Marlipal® O45/80.

Among these, particular preference is given to aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides, for example N-(3-dimethylaminopropyl)methacrylamide (DMAPMAM), and hydroxyalkyl (meth)acrylates, for example 2-hydroxyethyl methacrylate (HEMA).

Very particularly preferred mixtures for preparing the polymeric structure improvers comprise methyl methacrylate, butyl methacrylate, lauryl methacrylate, stearyl methacrylate and/or styrene.

These components may be used individually or as mixtures.

The preferred polymeric structure improvers generally have a molecular weight in the range from 10 000 to 1 000 000 g/mol, preferably in the range from 15×10^3 to 500×10^3 g/mol and more preferably in the range from 20×10^3 to 300×10^3 g/mol, without intention that this should impose a restriction. These values relate to the weight-average molecular weight of the polydisperse polymers in the composition. This parameter can be determined by gel permeation chromatography in a known manner.

The preparation of the polymeric structure improvers from the above-described compositions is known per se. For instance, these polymers can be effected especially by free-radical polymerization, and also related processes, for example ATRP (= atom transfer radical polymerization) or RAFT (= reversible addition fragmentation chain transfer).

The customary free-radical polymerization is explained, inter alia, in Ullmanns's Encylopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator is used for this purpose.
These include the azo initiators well 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 peroxyisopropylcarbonate, 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 also mixtures of the aforementioned compounds with compounds which have not been mentioned and can likewise form free radicals.

The ATRP process is known per se. It is assumed that it is a "living" free-radical polymerization, without any intention that this should restrict the description of the mechanism. In these processes, a transition metal compound is reacted with a compound which has a transferable atom group. This transfers the transferable atom group to the transition metal compound, which oxidizes the metal. This reaction forms a radical which adds onto ethylenic groups. However, the transfer of the atom group to the transition metal compound is reversible, so that the atom group is transferred back to the growing polymer chain, which forms a controlled polymerization system. The structure of the polymer, the molecular weight and the molecular weight distribution can be controlled correspondingly.

This reaction is described, for example, by J-S. Wang, et al., J. Am. Chem. Soc., vol. 117, p. 5614-5615 (1995), by Matyjaszewski, Macromolecules, vol. 28, p. 7901-7910 (1995). In addition, the patent applications WO 96/30421, WO 97/47661, WO 97/18247, WO 98/40415 and WO 99/10387 disclose variants of the ATRP explained above.

In addition, the inventive polymers may be obtained, for example, also via RAFT methods. This process is presented in detail, for example, in WO 98/01478, to which reference is made explicitly for the purposes of disclosure.

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 0° - 130°C and more preferably 60° - 120°C.

The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense.

The polymerization is preferably carried out in a nonpolar solvent. These include hydrocarbon solvents, for example aromatic solvents such as toluene, benzene and xylene, saturated hydrocarbons, for example cyclohexane, heptane, octane, nonane, decane, dodecane, which may also be present in branched form. These solvents may be used individually and as a mixture. Particularly preferred solvents are mineral oils, natural oils and synthetic oils, and also mixtures thereof. Among these, very particular preference is given to mineral oils.

The polymeric structure improvers may be random copolymers. In addition, these polymers may be graft polymers and/or block copolymers.

In a particular aspect of the present invention, the polymeric structure improver is obtainable by graft polymerization, in which case a composition comprising components a) to d) is polymerized onto a graft base which comprises an olefin copolymer (OCP) which has been formed predominantly from ethylene and propylene and/or a hydrogenated copolymer (HSD) formed from dienes and styrene.

The polyolefin copolymers (OCP) usable for this purpose are known per se. They are primarily polymers formed from ethylene, propylene, isoprene, butylene and/or further olefins having from 5 to 20 carbon atoms. It is equally possible to use systems which are grafted with small amounts of oxygen- or nitrogen-containing monomers (for example from 0.05 to 5% by weight of maleic anhydride). The copolymers which comprise diene components are generally hydrogenated in order to reduce the oxidation sensitivity and the crosslinking tendency of the polymers.

The molecular weight Mw is generally from 10 000 to 300 000, preferably between 50 000 and 150 000. Such olefin copolymers are described, for example, in the German published specifications DE-A 16 44 941, DE-A 17 69 834, DE-A 19 39 037, DE-A 19 63 039 and DE-A 20 59 981.

Ethylene-propylene copolymers are particularly useful, as are terpolymers with the known "ter" components, such as ethylidene-norbornene (cf. Macromolecular Reviews, Vol. 10 (1975)), but their tendency to crosslink in the course of the aging process needs to be taken into account. The distribution may be substantially random, but it is also possible advantageously to employ sequence polymers with ethylene blocks. The ratio of the ethylene-propylene monomers is variable within certain limits, which may be set at about 75% for ethylene and about 80% for propylene as the upper limit. Owing to its reduced tendency to solubility in oil, polypropylene is already less suited than ethylene-propylene copolymers. In addition to polymers with predominantly atactic propylene incorporation, it is also possible to use those having more marked iso- or syndiotactic propylene incorporation.

Such products are commercially available, for example, under the tradenames Dutral® CO 034, Dutral® CO 038, Dutral® CO 043, Dutral® CO 058, Buna® EPG 2050 or Buna® EPG 5050.

The hydrogenated styrene-diene copolymers (HSD) are likewise known, these polymers being described, for example, in DE 21 56 122. They are generally hydrogenated isoprene- or butadiene-styrene copolymers. The ratio of diene to styrene is preferably in the range from 2:1 to 1:2, more preferably approx. 55:45. The molecular weight Mw is generally from 10 000 to 300 000, preferably between 50 000 and 150 000. The fraction of the double bonds after the hydrogenation is, in a particular aspect of the present invention, at most 15%, more preferably at most 5%, based on the number of double bonds before the hydrogenation.

Hydrogenated styrene-diene copolymers may be obtained commercially under the tradenames ®SHELLVIS 50, 150, 200, 250 or 260.

The preparation of the graft copolymers which have been detailed above and have at least one HSD and/or OCP block and at least one block comprising the above-described components a), b), c) and/or d) is known in the technical field. For example, the preparation can be effected by means of polymerization in solution. Such processes are described, inter alia, in DE-A 12 35 491, BE-A 592 880, US-A 4 281 081, US-A 4 338 418 and US-A-4,290,025.

The polymeric structure improver is present in the lubricating grease preferably in an amount in the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, based on the total weight.

The lubricant oils which are present in the inventive lubricating greases include especially mineral oils, synthetic oils and natural oils.

Mineral oils are known per se and commercially available. They are generally obtained from petroleum or crude oil by distillation and/or refining and optionally further purification and finishing processes, the term petroleum including in particular the higher-boiling fractions of crude or petroleum. 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. Mineral oils are also produced in a smaller proportion from raw materials of vegetable (for example from jojoba, rapeseed) or animal (for example neatsfoot oil) origin. 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 fraction 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 from 0.5 to 30% by weight of aromatic fractions, from 15 to 40% by weight of naphthenic fractions, from 35 to 80% by weight of paraffin-base fractions, up to 3% by weight of n-alkanes and from 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 from approx. 18 to 31 carbon atoms:
0.7-1.0%,
slightly branched alkanes having from 18 to 31 carbon atoms:
1.0-8.0%,
aromatics having from 14 to 32 carbon atoms:
0.4-10.7%,
iso- and cycloalkanes having from 20 to 32 carbon atoms:
60.7-82.4%,
polar compounds:
0.1-0.8%,
loss:
6.9-19.4%.

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

Synthetic oils include organic esters, for example diesters and polyesters, polyalkylene glycols, polyethers, synthetic hydrocarbons, especially polyolefins, among which preference is given to polyalphaolefins (PAO), silicone oils and perfluoroalkyl ethers. 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.

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

The lubricating grease comprises preferably from 69.9 to 98.9% by weight, in particular from 75 to 95% by weight of lubricant oil, based on the total weight.

The thickeners present in the inventive lubricating greases are known per se in the technical field and can be obtained commercially. These are, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, Vol. 20, 2003, Wiley, ISBN 3-527-30385-5, in T. Mang and W. Dresel, Lubricants and Lubrication, 2001, Wiley, ISBN 3-527-29536-4, and Wilfried J. Bartz et al., Schmierfette, expert-Verl., 2000, ISBN 3-8169-1533-7. These include in particular soap thickeners, inorganic thickeners and polymeric thickeners.

The soap thickeners comprise generally at least one metal component and at least one carboxylic acid anion component.

The customary metal components include in particular the alkali metals such as lithium, sodium and potassium, the alkaline earth metals such as calcium or barium, and aluminum.

The carboxylic acid anion component comprises generally anions which are derived from long-chain carboxylic acids which in many cases have from 6 to 30 carbon atoms. These include in particular stearic acid, 12-hydroxystearic acid, octadecanoic acid, eicosanoic acid and hexadecanoic acid.

In addition, the carboxylic acid anion component may comprise anions which are derived from short-chain carboxylic acids having from 1 to 6 carbon atoms or from aromatic carboxylic acids. These include in particular acetic acid, propanoic acid and butanoic acid, and also benzoic acid.

The soap thickeners may be used as such in the process in order to produce a dispersion comprising grease structure. In addition, they may also be prepared in situ from the corresponding acids or their derivatives, for example their esters, and basic metal compounds.

The preferred acids have been detailed above. With regard to the esters, it should be emphasized that preference is given to esters having a short-chain alcohol radical having from 1 to 6 carbon atoms, for example the methyl, ethyl, propyl and/or butyl esters.

The preferred basic compounds include in particular the oxides, hydroxides and carbonates of the aforementioned metals.

The preferred soap thickeners include lithium 12-

hydroxystearate, lithium complex soaps, aluminum complex soaps and calcium complex soaps.

Furthermore, the basic compounds may also be added in an excess or deficiency for the preparation of the soaps to form underbased or overbased compounds.

Furthermore, inorganic thickeners can be used. These include in particular organophilic clays which may be derived from bentonite, and silica gel.

In addition, it is also possible to use polymeric thickeners. These include polyureas and thermoplastic powders such as polytetrafluoroethylene and fluoroethylenepropylene.

The lubricating grease comprises preferably from 0.01 to 30% by weight, more preferably from 0.2 to 15% by weight and most preferably from 0.5 to 10% by weight of thickeners, based on the total weight.

The weight ratio of lubricating oil to thickener in the lubricating grease is generally in the range from 100:1 to 100:30, preferably from 100:2 to 100:25, in particular from 100:5 to 100:15.

In addition, the inventive lubricating grease may comprise further additives.

These additives include viscosity index improvers, antioxidants, aging protectants, wear protectants, corrosion inhibitors, detergents, dispersants, EP additives, friction modifiers, dyes, odorants, metal deactivators and/or demulsifiers.

An inventive lubricating grease preferably has a water resistance of from 1 to 50%, more preferably in the range from 5 to 35%. The cone penetration of preferred lubricating greases is in the range from 175 to 385 dmm, more preferably in the range from 220 to 340 dmm.

The water resistance can be determined to ASTM D 4049. The cone penetration can be measured to ASTM D 1403.

In a particular aspect of the present invention, particular lubricating greases can be used at very low temperatures. The lubricating greases can preferably be used below a temperature of 0°C, more preferably of -10°C. Preferred greases can also be used at high temperatures of at least 50°C, more preferably at least 90°C.

The inventive lubricating greases can be produced on the basis of the customary processes, and these can be taken from the aforementioned prior art.

In general, the lubricating grease structure or lubricating grease matrix is obtained by physicochemical processes in a structure formation phase. In the course of this, various processes proceed, for example the aggregation of the thickener crystals, the formation of soap micelles by inclusion and adsorption of base oil molecules, the commencement of melting of the soap micelles (= heating above the melting point of the soap molecules) and finally the recrystallization of the soap molecules (= controlled cooling).

In many cases, a metal soap is obtained from precursors in a first stage. In the reaction phase, metal soap molecules are obtained by reaction of the corresponding starting materials in the base oil. The metal soap molecules are present in the form of fine crystals. This stage is optional, since it is not necessary by virtue of selection of appropriate precursor compounds.

The polymeric structure improver can be added before, during or after the structure formation phase. For example, the polymeric structure improver can be prepared initially in a mineral oil. Subsequently, a thickener or precursor compounds for preparing the thickener can be added to the resulting mixture.

Furthermore, the polymeric structure improver can be added after the structure formation phase, for example to a lubricating grease. The polymeric structure improver is preferably added in a composition liquid at 25°C to a dispersion which has a grease structure.

The term "grease structure" is known in the technical field, and this structure can be described as sponge-like. The structure of the dispersion can be demonstrated, for example, by microscopic images, the lubricating oil being kept within a thickener.

The composition may either be a dispersion or a solution. Accordingly, these compositions comprise at least one liquid medium.

The particularly preferred media include in particular lubricating oils which can likewise be used to prepare the dispersion which comprises at least one thickener and at least one lubricating oil.

Liquid media for dispersion or dissolution of the above-described polymeric structure improvers are known per se, and these media should be compatible with the dispersion which comprises at least one thickener and at least one lubricating oil. Compatibility is understood here to mean the miscibility of the medium with the dispersion which comprises at least one thickener and at least one lubricating oil.

In a particular aspect of the present invention, the composition which is liquid at 25°C and comprises at least one polymeric structure improver has a viscosity at 25°C in the range from 0.01 mm^2/s to 100 000 mm^2/s, preferably from 0.1 mm^2/s to 20 000 mm^2/s and more preferably from 1 mm^2/s to 10 000 mm^2/s to DIN 51562.

The concentration of the polymeric structure improver in the composition liquid at 25°C is preferably in the range from 1 to 99% by weight, more preferably in the range from 5 to 89% by weight and most preferably in the range from 10 to 80% by weight, based on the total weight of the composition.

The ratio of the weight of the dispersion to the weight of the composition which is liquid at 25°C and comprises at least one polymeric structure improver is preferably in the range from 100:1 to 1:1, more preferably in the range from 50:1 to 5:1 and most preferably in the range from 25:1 to 10:1.

The composition liquid at 25°C can be added, inter alia, during a mechanical phase which follows the structure formation phase.

Furthermore, the composition liquid at 25°C can be added to a finished lubricating grease after the mechanical phase. As a result of this particular aspect of the present invention, it is possible, for example, to produce a large amount of a simple lubricating grease which can subsequently be adjusted in a further step to the particular requirements of the final customer by the addition of the composition which is liquid at 25°C and may comprise further additives. As a result of this, particularly economically viable preparation of small amounts of specific lubricating greases is possible.

In a particular embodiment of the present invention, the water resistance can be improved by at least 30%, more preferably by at least 50% and most preferably by at least 70%, based on the water resistance of the dispersion to which the composition liquid at 25°C is added.

In a particular aspect of the present invention, the dispersion comprising grease structure and the composition liquid at 25°C are essentially biodegradable. This is measured to RAL-ZU 64.

The composition liquid at 25°C can be added to the dispersion comprising grease structure by commonly known methods.

These include stirring, mixing, kneading, rolling and/or homogenizing.

The temperature at which the composition liquid at 25°C is added to the dispersion comprising grease structure is not critical per se. At a high temperature, the composition liquid at 25°C can frequently be incorporated more easily into the dispersion. However, the grease structure must be stable at the addition temperature.

The composition liquid at 25°C is preferably added to the dispersion comprising grease structure at a temperature which is below the dropping point of the dispersion before the addition of the liquid composition. The dropping point can be determined to ASTM D 2265.

More preferably, the composition liquid at 25°C is added to the dispersion comprising grease structure at a temperature which is at least 40°C, most preferably at least 60°C, below the dropping point of the dispersion before the addition of the liquid composition.

In a preferred variant of the process according to the invention, the composition liquid at 25°C can be added at a temperature in the range from 0°C to 75°C, in particular in the range from 25°C to 70°C.

The invention will be illustrated in detail below by examples and comparative examples, without any intention that the invention be restricted to these examples.

The following abbreviations are used below.

KV 100, KV 40 = kinematic viscosity, measured to DIN 51562 at 100°C and 40°C

Typically, the polymer solutions described in the examples are analyzed in a 150 N test oil; the number in () indicates the polymer concentration used.

[η] denotes the limiting viscosity number measured to DIN ISO 16281, part 6.

Preparation example 1
Preparation of PAMA/methacrylic acid polymers

In a 2 l four-neck flask equipped with stirrer, thermometer and reflux condenser, 6.1 g of methacrylic acid and 603.9 g of a C10-C18-alkyl methacrylate are dissolved in 499 g of 100 N oil, for example 100 SN from Kuwait Petroleum. The solution is inertized by means of addition of 10 g of dry ice and the temperature is subsequently increased to 82°C. On attainment of the temperature, the polymerization is initiated by adding 0.73 g of initiator (tert-butyl per-2-ethylhexyl hexanoate). 1.21 g of initiator are added after 4 hours of reaction time and 111 g of 100 N oil are added after a further 4 hours. The resultant polymer solution is approx. 50% strength.

KV 100 (2% strength in 150 N oil): 10.11 mm^2/s

KV 40 (2% strength in 150 N oil): 58.43 mm^2/s

[η] 136 cm^3/g

Preparation example 2
Preparation of a PAMA polymer without acid function

Preparation analogous to Example 1
Batch polymerization, 82°C, 55% in 100 N oil
495.0 g of 100 N oil
605.0 g of C12-C18 alkyl methacrylate
0.73 g of initiator (0.12%)
Replenishment step (after 4 h): 1.21 g of initiator (0.20%)
Dilution to 50% with 110.0 g of 100 N oil
KV 100 (2% strength in 150 N oil): 9.98 mm^2/s
KV 40 (2% strength in 150 N oil): 55.58 mm^2/s
[η] 127 cm^3/g

Preparation example 3:
Preparation of an NLGI grade 2 Li soap grease (EG 2768)

A 6 l lubricating grease autoclave tank equipped with oil jacket heating and a mechanical planetary stirrer is charged with 272 g of hydrogenated castor oil (HCO, 181.6 mg KOH/g), 40 g of lithium hydroxide, 32 g of Vanlube™ NA (a diphenylamine from Vanderbilt), 32 g of Lubad 199™ (a calcium salicylate from Shell), and 1440 g of HVI 650 oil from Shell and 1330 g of HVI 160 oil from Shell. The tank is closed and kept at 100°C/100 rpm for one hour. Subsequently, the water of reaction formed is discharged and the mixture is heated to 210°C. On attainment of the peak temperature, the mixture is cooled to 165°C at a rate of 1°C/min at 200 rpm. Subsequently, the mixture is cooled further to a temperature of 50°C at 100 rpm. The tank is opened and the grease formed is homogenized at least twice by means of a three-roll mill, and transferred into a bucket.

Physical data:
Cone penetration (IP 50) unprocessed: 285 dmm, 288 dmm after 60 motions (NLGI grade 2), 317 dmm after 100 060 motions.

Dropping point (ASTM D566): 197.7°C
Water wash-out (ASTM D 1264): 7.5%
Water spray-off (ASTM D 4049): 33.8%

Example 1

In a mixer (Kenwood Chef), 990 g of the lubricating grease EG 2768 of classification NLGI grade 2 based on Li soaps, obtainable according to preparation example 3, were mixed at 60°C with 10 g of a solution which comprises 50% by weight of polymers having acid groups which have been obtained according to preparation example 1 and a lubricant oil. The resulting mixture was subsequently homogenized by means of a three-roll mill (Exact 50 from Exact Apparatebau). The properties of the modified lubricating grease were determined below.

For this purpose, more particularly, the dropping point was measured to ASTM D 566, cone penetration to ASTM D 217 and water resistance to ASTM D 4049. The data obtained are presented in Table 1.

Comparative example 1

Example 1 was essentially repeated, except that no solution was incorporated. The data obtained are presented in Table 1.

Comparative example 2

Example 1 was essentially repeated, except that a solution was incorporated which comprises 50% by weight of polymers without acid groups which have been obtained according to preparation example 2. The data obtained are presented in Table 1.

Table 1

	Cone penetration after 60 motions	Dropping point	Water resistance	Improvement based on original grease
Ex. 1	291	197°C	20%	41%
Comp.Ex. 1	288	198°C	34%	-
Comp.Ex. 2	279	198°C	27%	21%

Example 2

In a mixer (Kenwood Chef), 990 g of the lubricating grease Farmlub™ of classification NLGI grade 2 based on Li soaps, obtainable from F&S Mannheim, were mixed at 60°C with 10 g of a solution which comprises 50% by weight of polymers with acid groups which have been obtained according to preparation example 1 and a lubricant oil. The resulting mixture was subsequently homogenized by means of a three-roll mill (Exact 50 from Exact Apparatebau). The properties of the modified lubricating grease were determined below.

To this end, more particularly, the dropping point was determined to ASTM D 566, cone penetration to ASTM D 217 and water resistance to ASTM D 4049. The data obtained are presented in Table 2.

Comparative example 3

Example 2 was essentially repeated, except that no solution was incorporated. The data obtained are presented in Table 2.

Example 3

Example 2 was essentially repeated, except that 40 g of the dispersion which comprises 50% by weight of polymers having acid groups which have been obtained according to preparation example 1 and a lubricating oil were incorporated into 960 g of lubricating grease from F&S Mannheim. The data obtained are presented in Table 2.

Comparative example 4

Example 2 was essentially repeated, except that 10 g of a solution which comprises 50% by weight of polymers without acid groups which have been obtained according to preparation 2 and a lubricating oil were incorporated. The data obtained are presented in Table 2.

Comparative example 5

Example 3 was essentially repeated, except that 20 g of a solution which comprises 50% by weight of polymers without acid groups which have been obtained according to preparation example 2 and a lubricating oil were incorporated into 980 g of grease from F&S. The data obtained are presented in Table 2.

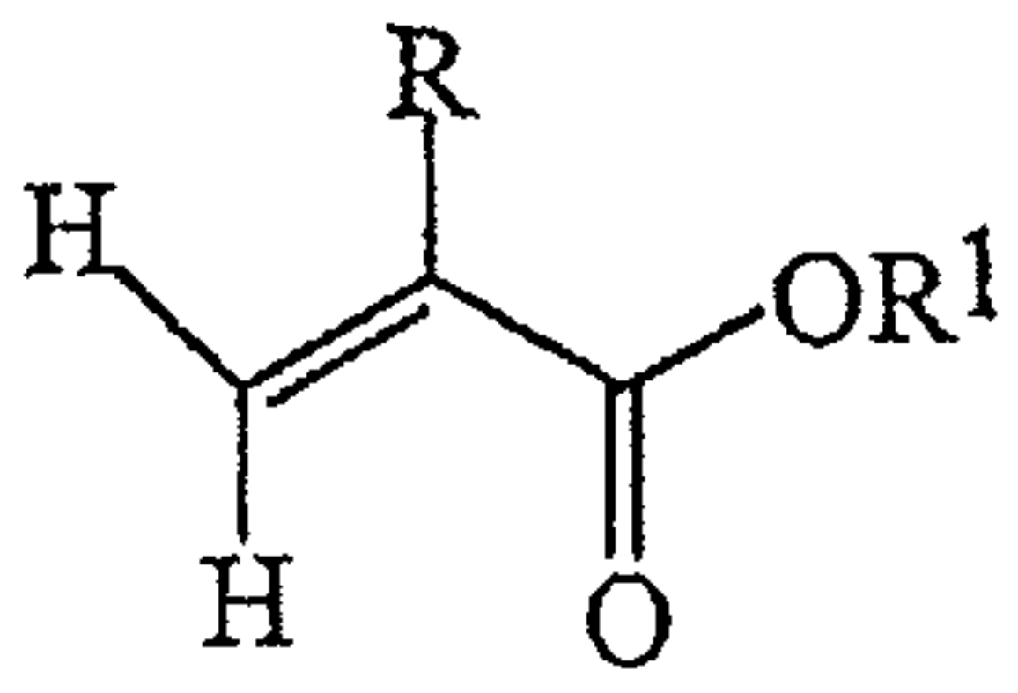
Table 2

	Cone penetration after 60 motions	Dropping point	Water resistance	Improvement based on original grease
Ex. 2	291	182°C	20%	68%
Comp.Ex. 3	251	186°C	62%	-
Ex. 3	294	185°C	11%	82%
Comp.Ex. 4	-	188°C	40%	35%
Comp.Ex. 5	-	183°C	28%	55%

What is claimed is:

1. A lubricating grease comprising at least one thickening agent, at least one lubricating oil, and at least one polymeric structure improver obtained by polymerization of monomer compositions, which comprise

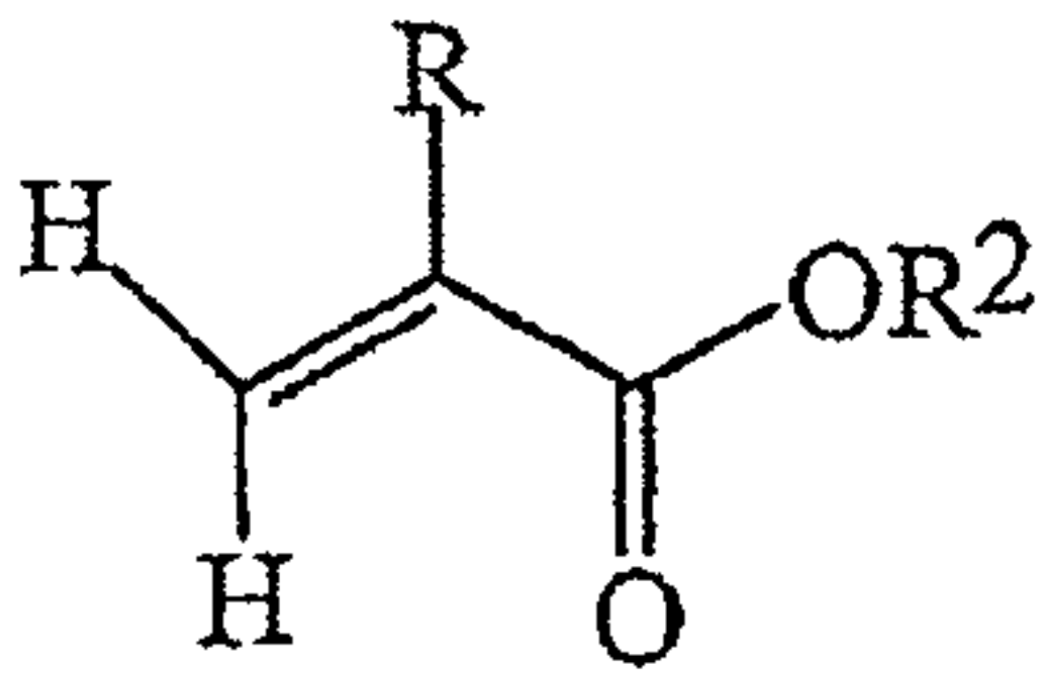
a) optionally, 0 to 40 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of at least one (meth)acrylate of formula (I)



(I),

in which R represents hydrogen or methyl, R^1 denotes a straight-chain or branched alkyl moiety having 1 to 5 carbon atoms,

b) 40 to 99.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of at least one (meth)acrylate of formula (II)



(II),

in which R represents hydrogen or methyl, R^2 denotes a straight-chain or branched alkyl moiety having 6 to 30 carbon atoms,

c) 0.01 to 5 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of monomers containing acid groups or salts thereof,

d) optionally, 0 to 59.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of comonomer.

2. A lubricating grease according to claim 1, wherein at least part of the monomers according to component c) contains at least one carboxyl group, at least one phosphonic acid group, at least one sulfonic acid group, a combination thereof or salts thereof.

3. A lubricating grease according to claim 2, wherein component c) contains at least one monomer selected from the group comprising methacrylic acid, acrylic acid, a combination thereof or salts thereof.

4. A lubricating grease according to claim 1, wherein the monomer composition contains 0.1 to 5 wt % relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of monomers containing acid groups or salts thereof according to component c).

5. A lubricating grease according to claim 1, wherein the polymeric structure improver has a weight-average molecular weight ranging from 15,000 g/mol to 1,000,000 g/mol.

6. A lubricating grease according to claim 1, wherein the thickener is a soap thickener, an inorganic thickener, a polymeric organic thickener or a combination thereof.

7. A lubricating grease according to claim 1, wherein the lubricating grease further comprises additives.

8. A lubricating grease according to claim 1, wherein the lubricating grease has a water resistance of 1 to 50%.

9. A lubricating grease according to claim 1, wherein the lubricating grease has a cone penetration ranging from 175 dmm to 385 dmm.

10. A lubricating grease according to claim 1, wherein the polymeric structure improver contains a block copolymer.

11. A lubricating grease according to claim 10, wherein the polymeric structure improver is obtained by graft polymerization, wherein a composition comprising components a) to d) is polymerized on a graft base, which comprises an olefin copolymer (OCP) formed predominantly from ethylene and propylene or a hydrogenated copolymer (HSD) of dienes and styrene.

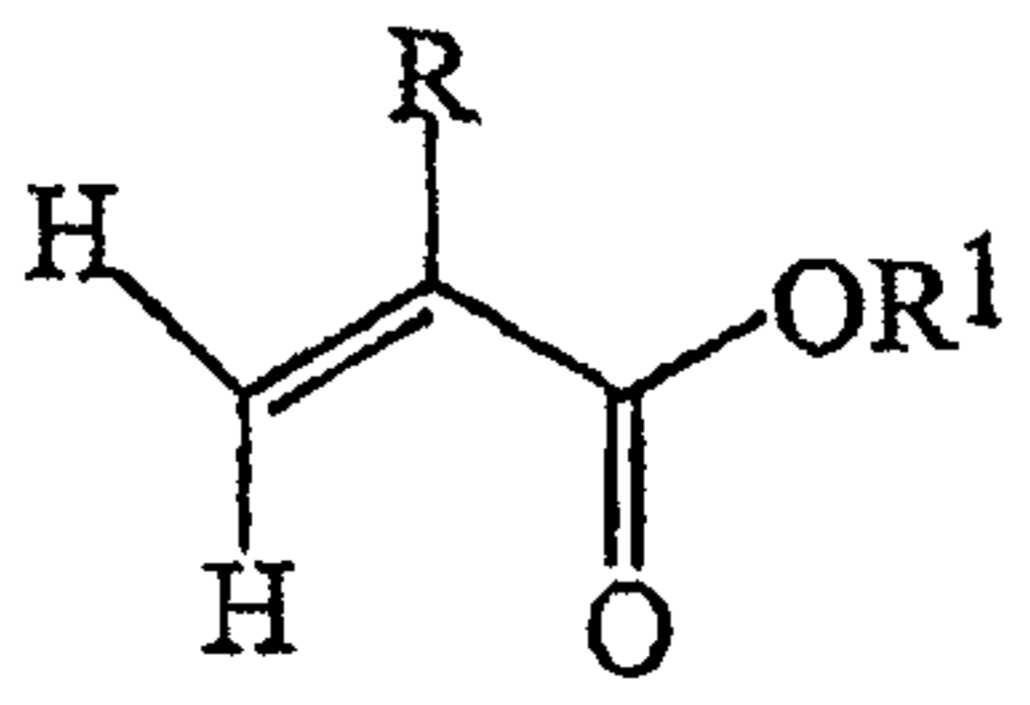
12. A lubricating grease according to claim 10, wherein the polymeric structure improver is obtained by graft polymerization, wherein a composition comprising components a) to d) is polymerized on a graft base, which comprises an olefin copolymer (OCP) formed predominantly from ethylene and propylene and a hydrogenated copolymer (HSD) of dienes and styrene.

13. A lubricating grease according to claim 1, wherein the lubricating grease contains 1 to 30 wt % of thickener.

14. A lubricating grease according to claim 1, wherein the lubricating grease contains 69.9 to 98.9 wt % of lubricating oil.

15. A method for production of lubricating grease, comprising producing a mixture comprising at least one thickening agent, at least one lubricating oil and a polymeric structure improver, which is obtained by polymerization of monomer compositions, which comprise

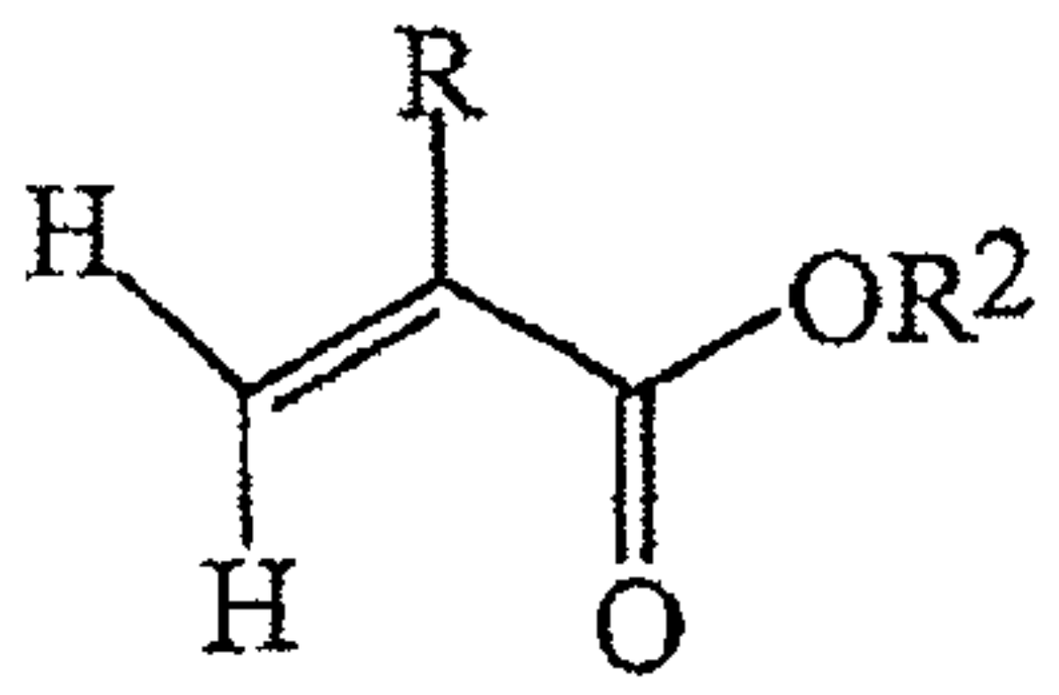
a) optionally, 0 to 40 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of one or more ethylenically unsaturated ester compounds of formula (I)



(I),

in which R represents hydrogen or methyl, R^1 denotes a straight-chain or branched alkyl moiety having 1 to 5 carbon atoms,

b) 40 to 99.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of one or more ethylenically unsaturated ester compounds of formula (II)



(II),

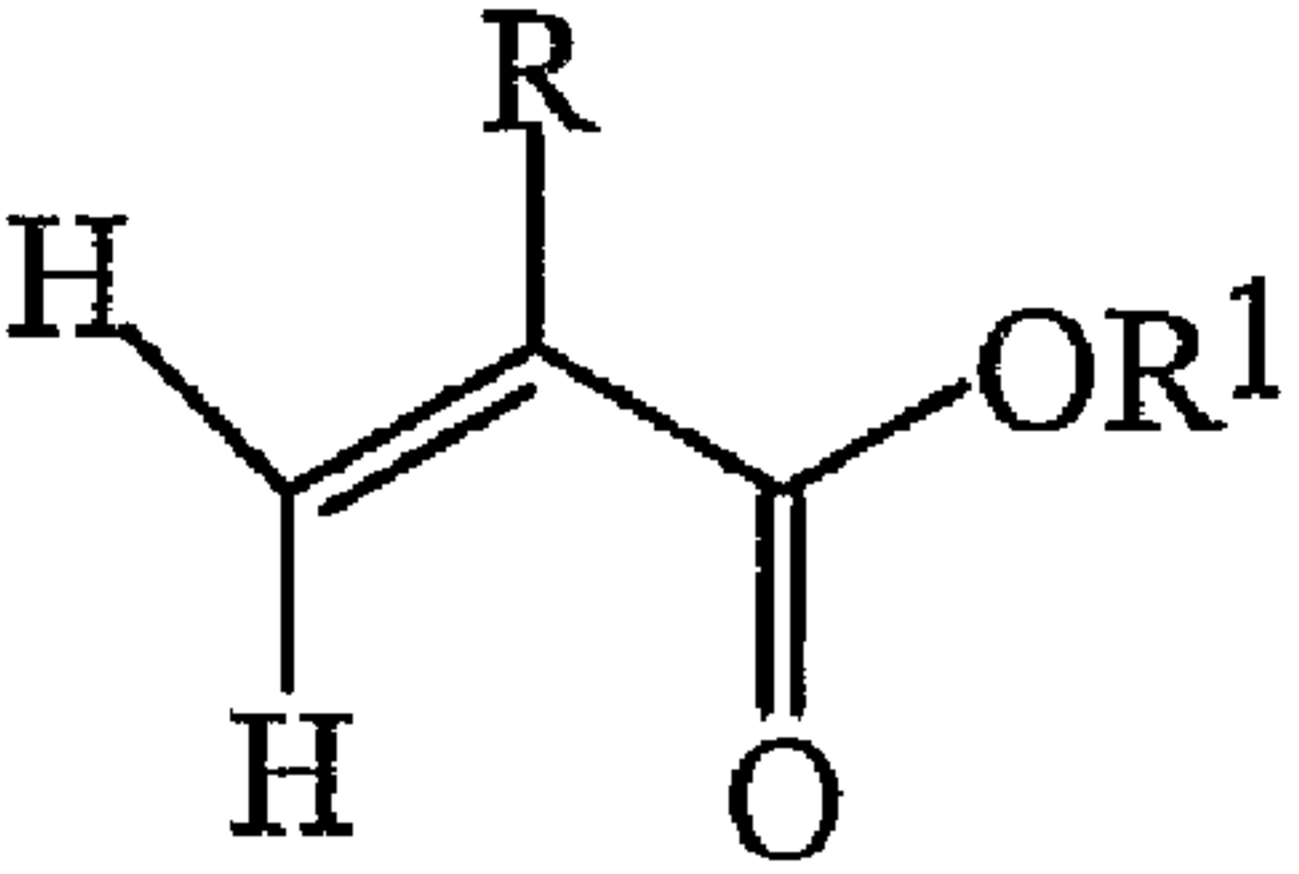
in which R represents hydrogen or methyl, R^2 denotes a straight-chain or branched alkyl moiety having 6 to 30 carbon atoms,

c) 0.01 to 20 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of monomers containing acid groups or salts thereof,

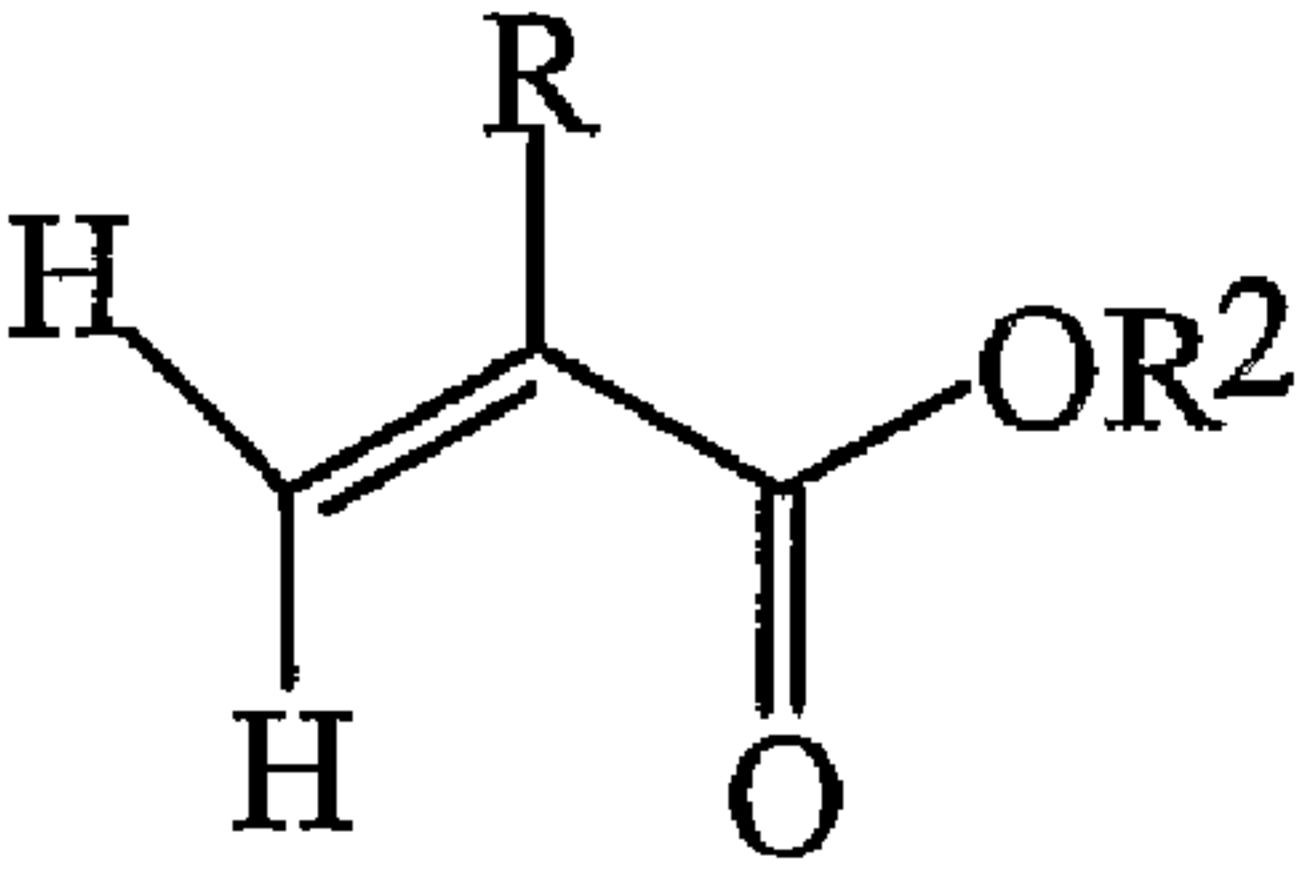
d) optionally, 0 to 59.99 wt %, relative to the weight of the monomer compositions for synthesis of the polymeric structure improvers, of comonomer.

16. A method according to claim 15, wherein the polymeric structure improver is added to a dispersion that has a grease structure and that comprises at least one thickening agent and at least one lubricating oil.

17. A method according to claim 15, wherein the polymeric structure improver is added in a composition that is liquid at 25°C.



(I)



(II)