

Graft polymers and their use as lubricant additives

- 5 The invention relates to graft polymers obtained from macromonomers and which may be used as lubricant additives with a viscosity index improving and dispersing action.
- 10 Prior art comb polymers which are used, for example, as polymeric stabilisers in emulsions, have been known for some time (cf. G. Allen, J.C. Bevington, Comprehensive Polymer Science Vol. 4, pg. 248 - 250, Pergamon Press 1989).
- 15 Such comb polymers may be obtained by the radically initiated copolymerisation of macromonomers with (chemically different) comonomers. US-A 5,254,632 discloses a relatively simple method for preparing
- 20 suitable macromonomers in which (meth)acrylic acid esters are polymerised in the presence of a hydroxy group-containing sulphur regulator, and the resultant hydroxyl group-terminated polyalkyl (meth)acrylates are transesterified with methyl methacrylate to form
- 25 poly(meth)acrylate macromonomers having a methacryloyl terminal group. The US patent also discloses a list of relevant literature references in which, inter alia, various methods of preparing macromonomers are described.
- 30 The comb polymers obtainable by the above methods may be used for a number of different applications. Due to their structures, their use as emulsifiers is of particular interest. However, the structural features
- 35 do not necessarily suggest that such copolymers would be particularly suitable as viscosity index improvers (VI-improvers) in lubricating oils. There is, however, a clear need for effective VI-improvers as lubricant

additives, especially for those which also have a dispersive action.

5 It has now been found that the lubricant additives according to the invention, which are based on certain comb polymers, are especially suitable for use in lubricant technology. Thus the invention relates to lubricant oil additives comprising graft polymers PFP as VI-improving agents. The graft polymers are synthesised
10 from polyalkyl methacrylate macromonomers (A), which are copolymerised in a carrier medium TM with alkyl (meth)acrylic acid esters comprising C₆-C₃₀-alkyl groups (AMA), with non-functionalised comonomers (B) selected from the group comprising alkyl (meth)acrylic acid
15 esters comprising C₁-C₅-alkyl groups, styrene and alkyl styrenes comprising C₁-C₄-alkyl groups, and vinyl esters, and with functionalised comonomers (C) selected from the group comprising (meth)acrylic acid esters, (meth)acrylamides and vinyl heterocycles.

20 Normally, the components from which the graft polymers PFP are synthesised are present in the following weight ratios: (sum of the parts generally = 100 wt.%)

25 macromonomers (A) = 10 - 90 wt.%,
alkyl(meth)acrylic acid esters having C₆-C₃₀-alkyl groups (AMA) = 0 - 90 wt.%,
non-functionalised comonomers (B) = 0 - 60 wt.% and
functionalised comonomers (C) = 0 - 40 wt.%.

30 In a preferred embodiment of the invention, the structure of the graft polymers PFP may be schematically illustrated by the following formula I,

35

wherein

R_1 denotes $-H$ or $-CH_3$,

R_2 denotes $-H$ or $-CH_3$,

20 R₃ denotes -H or -CH₃,

n = 6 to 30,

$m = 6$ to 30 ,

p = average polymerisation degree of the macromonomers
(A),

25 (-co- is the standard abbreviation of "copolymerised with").

When preparing graft polymers PFP, macromonomers of formula II are preferably used:

$$\begin{array}{c} \text{R}_1 \\ \diagup \\ \text{C} = \text{O} \\ \diagdown \\ \text{O} \end{array} - \text{X} - \left[\text{CH}_2 - \text{C} \begin{array}{c} \text{R}_2 \\ | \\ \text{O} = \text{C} \\ | \\ \text{OC}_n\text{H}_{2n+1} \end{array} \right]_p \text{H} \quad (\text{II})$$

wherein

X denotes a bivalent group,

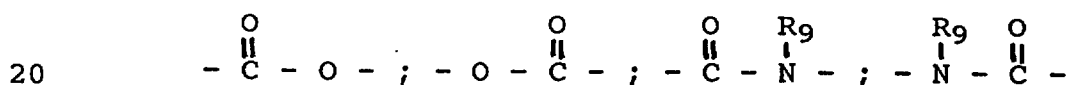
R₁ denotes -H or -CH₃,

R₂ denotes -H or -CH₃,

5 n = 6 to 30

p = average polymerisation degree of the macromonomers.

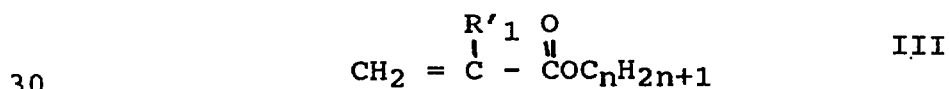
Here, p is preferably such that the molecular weight
average M_w of the macromonomers of formula II is within
10 the range 1,000 to 100,000. Preferably, the bivalent
group X is an at least 2 and up to 30-membered
hydrocarbon chain, preferably with a -S- bridge directly
adjacent to the polymer part of I, whilst optionally up
to 9 carbon atoms of the chain may be substituted by
15 oxygens in ether linkage. Furthermore, in the group X,
the chain may also be interrupted by functional groups
of formula



wherein R₉ is hydrogen or an alkyl group having 1 to 8
carbon atoms or a phenyl group.

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The alkyl(meth)acrylates AMA may generally be expressed
by formula III



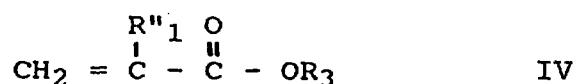
wherein

R'₁ denotes H or CH₃, and

n = 6 to 30

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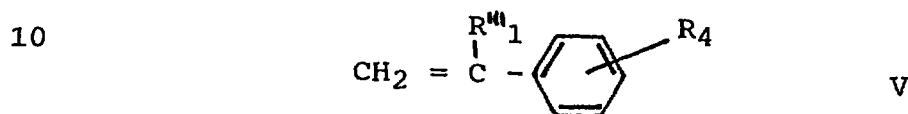
The comonomers (B) normally correspond to formula IV



wherein

- 5 R''_1 denotes H or CH_3 , and
 R_3 denotes C_1 - C_5 -alkyl, preferably C_1 - C_4 -alkyl,

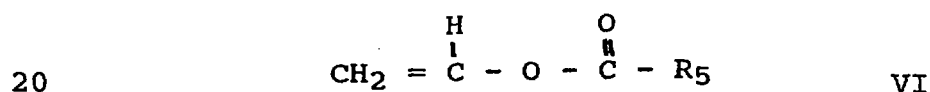
or to formula V



wherein

- R''_1 denotes H or CH_3 , and
 15 R_4 denotes H or C_1 - C_4 -alkyl,

or to formula VI



wherein

R_5 denotes C_1 - C_{11} -alkyl.

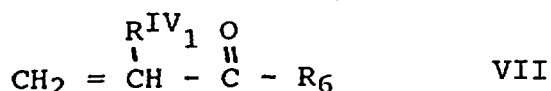
- 25 The comonomers of formula IV include, for example, -
 vinylacetate, vinylpropionate, vinylisobutyrate, vinyl-
 2-ethylhexoate and vinyl esters of coconut oil fatty
 acids or of C_{10} -oxo acids (cf. Kirk-Othmer, 3rd. Ed.,
 Vol. 4, 863 - 871, J. Wiley 1978).

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A preferred comonomer of formula IV is methyl
 methacrylate (monomer IV-a).

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The functionalised, especially dispersively active
 comonomers (C) (which are not identical with the above
 comonomers) may, preferably, be expressed by formula VII



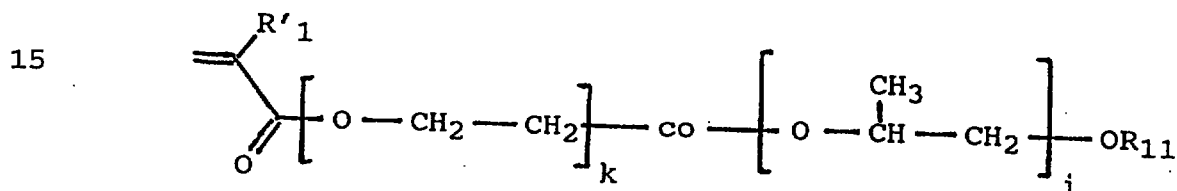
wherein R^{IV}_1 denotes hydrogen or methyl, R_6 denotes $-\text{OR}_9$ or $-\text{NR}_7\text{R}_8$ and wherein R_9 denotes an alkyl group having 2 to 20 carbon atoms which is substituted by at least one hydrophilic group A selected from the group comprising hydroxyl, an $-\text{NR}'_7\text{R}'_8$ group, a sulphonic acid group, a carboxyl or carboxamide group or a 5 to 6-membered heterocycle which is itself soluble in water, in which the carbon chain may be interrupted by ether bridges or terminated by a phenyl or phenoxy group optionally substituted by a C_1 - C_{12} -alkyl group, and wherein R'_7 and R'_8 may be hydrogen or an alkyl group having 1 to 6 carbon atoms which may optionally be substituted by a hydrophilic group A, or wherein R'_7 and R'_8 , optionally together with further nitrogen or oxygen atoms, may form a 5- or 6-membered heterocycle, and wherein R'_7 and R'_8 may be hydrogen or an alkyl group having 1 to 6 carbon atoms, whilst $-\text{NR}'_7\text{R}'_8$ may optionally be quaternised, or if R_7 is hydrogen, R_8 may be a carboxamido group.

Preferably, the functionalised comonomers (C) are selected from the group comprising optionally substituted (meth)acrylamide, hydroxy alkyl esters of (meth)acrylic acid such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, amine-substituted alkyl esters such as 2-diethylaminoethyl(meth)acrylate, 2-(1-imidazolyl)ethyl-(meth)acrylate, 2-(4-morpholinyl)ethyl(meth)acrylate, 2-trimethylammoniummethyl(meth)acrylate salts, hydroxalkyl substituted (meth)acrylamides such as N-(2-hydroxyethyl)(meth)acrylamide, N-(3-hydroxy-2,2-dimethylpropyl)(meth)acrylamide, N-dimethylaminomethyl(meth)acrylamide, N-(meth)acryloidpyrrolidon-2-, N-(meth)acrylamidomethylpyrrolidone, N-(1-piperidinylmethyl)-(meth)acrylamide, quaternary ammonium

compounds such as N-trimethylammoniumpropyl(meth)-acrylamide salts, sulphonic acid derivatives such as 2-(meth)acrylamido-2-methylpropane sulphonic acid or N-(meth)acryloylurea.

- 5 Particularly preferred monomers are 2-(N-morpholinyl)ethyl-methacrylate (= Monomer VII-a) and N-vinylpyrrolidone (= Monomer VIII-a).

10 Of special interest are monomers of formula VII wherein R_6 is an alkoxyated alkanol or phenyl group (comonomers of formula VII-A).



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VII-A

25 wherein

R'_1 denotes -H or -CH₃,

$k = 5$ to 100 ,

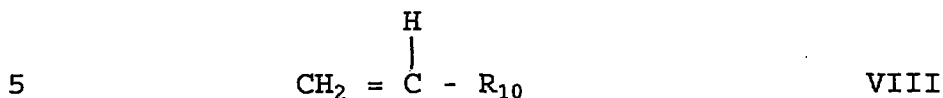
$i = 0$ to 100 ,

30 R_{11} denotes C_nH_{2n+1} , branched or unbranched, or an optionally substituted phenol, and
 $n = 1$ to 22 .

35 Comonomers of formula VII-A in which R_{11} is derived from industrial phenols or phenol mixtures are considered to be particularly suitable. In addition to phenol itself, mention must be made of tert.butylphenol, octylphenol, nonylphenol and dinonylphenol.

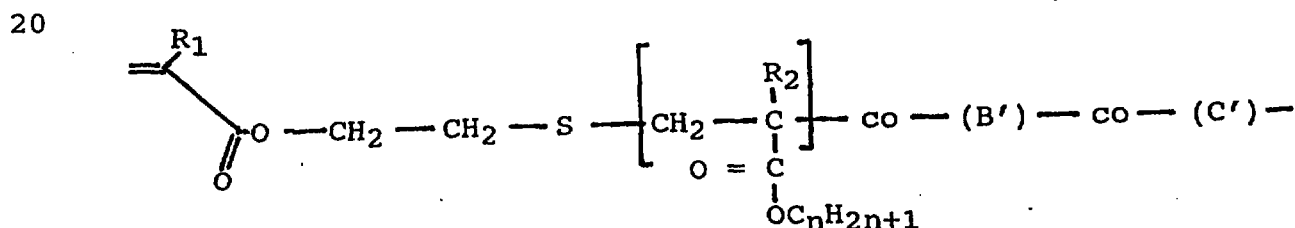
Furthermore, the functionalised comonomers (C) may

belong to the group of formula VIII



wherein R_{10} is a 5- or 6-membered heterocycle comprising at least one nitrogen atom. The comonomers of formula VIII are, preferably, selected from the group comprising vinylpyrrolidones such as 1-vinyl-2-pyrrolidone, vinylimidazole, N-vinylcarbazole, N-vinylsuccinimide, N-vinylloxazolidone, N-vinylphthalimide and vinylpyridines such as 2-vinylpyridine.

Functionalised poly(meth)acrylate macromonomers may also be used as starting products for preparing graft polymers (PFP). Preferably, these are macromonomers of formula II-A



wherein

R_1 denotes -H or -CH₃,

R_2 denotes -H or -CH₃,

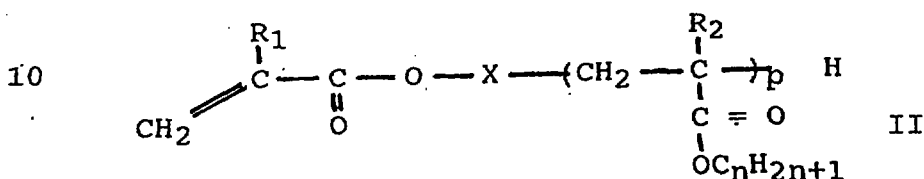
$n = 6$ to 30 ,

and wherein (B') denotes the same comonomers as (B), and (C') denotes the same comonomers as (C).

The molecular weight average (M_w) of the macromonomers is 1,000 to 100,000

The macromonomer II-A may comprise the following weight ratios: parts of AMA 0 - 90 wt.%, parts of comonomer (B') 0 - 40 wt.%, parts of (C') 0 to 100 wt.%.

5 Advantageously, the present invention may use the process for preparing macromonomers of general formula II



wherein R_1 and R_2 denote hydrogen or methyl

15 X denotes a bivalent group and

n is an integer of 5 to 30, with the proviso that p is such that the molecular weight M of the macromonomers II is within the range of 1,000 to 100,000 g/mol,

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according to DE-A 41 21 811 or US-A 5,254,632, in which monomeric esters of formula IX

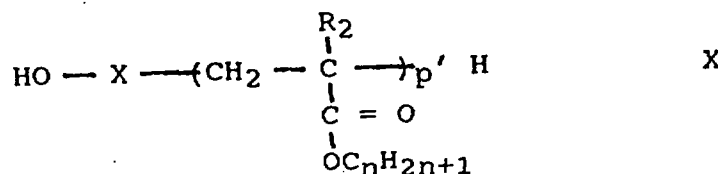
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wherein R_{12} is an alkyl group having 1 to 8 carbon atoms, are transesterified with a hydroxyl group-terminated polyalkylmethacrylate of formula X

30

35



wherein X, R₂ and n have the above meanings, with the proviso that p' corresponds to p after cleavage of the alcohol HOR₁₂ to form the compound of formula II.

5 The compounds of formula X are obtainable by the preferred methods of preparing macromonomers. Here, the monomers or monomer mixtures of (meth)acrylate esters are polymerised in the presence of an OH-functionalised regulator, preferably a sulphur regulator, for example
10 in the presence of 2-mercaptoethanol (cf. US-A 5,254,632). In the latter case, X denotes the structure -(CH₂)₂S-. However, other prior art methods may also be used successfully, which are suitable for preparing a PAMA-macromonomer with the same monomer composition
15 exhibiting relatively high functionality on a terminal polymerisable (activated) double bond (cf. EP 261 942).

Of special significance are macromonomers (A) synthesised from (meth)acrylic acid esters of
20 commercially available mixtures of alcohols in the claimed C₆-C₃₀ region, more particularly within the region of average C-numbers of about 10 to about 20, especially also within the region of about 12 to 18, more particularly within the region of 12.2 to 15.
25 These include, for example, the (meth)acrylic acid esters of a mixture of C₁₁-C₁₆-alcohols having an average C-number of 13.2 to 13.8 (commercial product DOBANOL 25L made by Shell AG).

30 The carrier medium TM for the graft polymers PFP may, preferably, be inert, preferably lipophilic, solvents of the kind normally employed in additive technology, especially mineral oils e.g. of the SN100 type such as Shell SM 920, or gas oils such as Shell G07.

35 The preparation of the macromonomers may be carried out in analogous processes to those of US-A 5,254,632 or according to DE-A-23 18 809; W. Radke, A.H.E. Müller,

Poly. Prepr. (Am. Chem. Soc. Div. Polym. Chem) 32(1)
1991 and H. Rauch-Puntigam, Th. Völker, Acryl- and
Methacrylverbindungen, Springer-Verlag 1967.

5 Preparing macromonomers (A)

- Preparing the hydroxyl group containing first stage

10 A mixture of alkyl(meth)acrylates AMA, together with a
molecular weight regulator such as mercaptoethanol
(about 1.0 wt.% based on the monomers, given as a guide)
are, advantageously, introduced into a suitable reaction
vessel such as a three-necked flask equipped with
heater, stirring device, internal thermometer, gas-feed
15 device and reflux cooler in e.g. 10 times the amount of
carrier medium TM, and the mixture is heated while
introducing such an inert gas such as nitrogen, for
example to 95°C. The initiator is then added, for
example a conventional per-compound such as a perester,
20 e.g. tert.butylper-2-ethylhexanoate, and the AMA monomer
is then added by metering, preferably mixed with a
further initiator (about 0.4 wt.% of initiator based on
the monomers, given as a guide) over about 3.5 hours.
After the end of the feed, at certain intervals, e.g.
25 after every 2.5 and 5 hours about half the amount of
initiator is, advantageously, added and, the mixture is
maintained over a longer period, for example 12 hours,
at 95°C. Thereupon, it is suitably diluted with the
carrier medium TM.

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- Transesterification

35 A mixture of the hydroxyl group-containing primary
product and methyl(meth)acrylate (in a weight ratio of
about 4.3 : 3, given as a guide), preferably in
combination with at least one known polymerisation
inhibitor e.g. hydroquinone monomethyl ether and a
stabiliser, for example of the HALS-type e.g. 4-hydroxy-

2,2,6,6-tetramethylpiperidine-1-oxide are introduced in the usual amounts into a suitable reaction vessel e.g. a 6 l three-neck flask equipped with heater, stirring device, internal thermometer, air inlet and packed column with a regulator-controlled vapour-inlet pipe, and the mixture is then suitably heated to refluxing while passing air through it. Hereinafter, MMA is expected to be the transesterification component. After a certain proportion has been transesterified, a transesterification catalyst, preferably a lithium compound such as lithium methoxide (about 0.1% based on the methylmethacrylate, given as a guide) is added, and the refluxing is further maintained until the boiling temperature decreases to about 65 to 68°C. Further methanol-rich distillate is then removed until the increase in boiling temperature, e.g. to about 100°C, shows that the reaction has largely taken place. After distilling further distillate (at 100°C), the preparation mixture is cooled to ambient temperature and filtered. Preferably, the excess methyl ester is removed on the vacuum rotation evaporator. The macromonomers A obtained are dissolved in the carrier medium TM.

25 Preparing a high molecular weight graft polymer PFP--

The macromonomers A, preferably obtained as described above, the AMA monomers and optionally the comonomer B are mixed in the required ratio. Carrier medium TM is added to the mixture. A small proportion of the mixture, for example 6.5 wt.% in about 10 times the amount of carrier medium, is used in an apparatus for preparing the hydroxyl group-containing primary product and heated to an elevated temperature (82°C as a guide), under an inert gas such as nitrogen. After adding a radical initiator to the preparation mixture, the further monomer mixture and the initiator are preferably pumped in continuously, over a certain time e.g. 3.5

hours. After a longer interval at the end of the feed, e.g. 12 hours, further initiator is added and left to react for a few hours, e.g. 8 hours, at an elevated temperature (about 82°C). The mixture is then suitably
5 diluted by adding the carrier medium TM (e.g. to an approximately 40% solution).

Preparing a dispersively active comb polymer

10 A macromonomer A, which preferably has a lower molecular weight, is introduced together with at least one dispersively active monomer C, preferably together with a regulator, especially a sulphur regulator (about 0.1
15 wt.% based on the macromonomers/monomers, given as a guide) are introduced to the above apparatus, and the mixture is heated, e.g. to 100°C, under an inert gas such as nitrogen, and initiator of e.g. the above kind is added in amounts of about 0.8 wt.%. At intervals of
20 a few hours e.g. after 3 and 7 hours, further initiator is suitably added, in batches of about 1/5 of the amount already added, and the mixture is further maintained at an elevated temperature, e.g. at 100°C, over a longer period of time, for example 12 hours.
25 Further advantageous variants of the preparation process may be deduced from the Examples.

The graft polymers PFP are noted for having an excellent activity as viscosity index improving agents. The
30 improved viscosity-temperature characteristics may be demonstrated on model formulations by way of viscosity measurements. The excellent dispersing action according to the invention is also of special importance. The highly advantageous dispersive effectiveness is
35 demonstrated, for example, by the results of laboratory tests.

The following Examples are non-limiting illustrations of

the invention. The actual viscosity is determined according to ASTM D 445. The molar weight is determined by size exclusion chromatography (SEC) using standard PMMA (cf. H.F. Mark et al. Encyclopedia of Polymer Science & Engineering, Vol. 10, pg. 1 - 19, J. Wiley 1987). The 100 N-oil used in the Examples is a shell SM 920.

The determination of the shear stability (shear stability index) PSSI is carried out according to ASTM D 2603 ref. B.

Examples

Preparing macromonomers A

5 A-1

Preparing a PAMA-macromonomer, $M_w = 19,000$.

a) Preparing the primary OH-substituted phase

10 A mixture is prepared from 1,170 g of the methacrylates
of a mixture of C_{11} - C_{16} -alkanols (product DOBANOL 25L
made by SHELL AG) and 11.7 g of 2-mercaptoethanol. 14.4
g of this monomer mixture and 130 g of 100 N-oil are
introduced into a 4 l three-necked flask equipped with
15 oil bath heater, internal thermometer, N_2 transfer pipe
and reflux cooler, and the mixture is heated to 95°C.
After adding 1.18 g tert.-butylper-2-ethylhexanoate as
initiator, a mixture of 1,167.3 g of C_{11-18} -methacrylates
and 3.5 g of initiator is uniformly added by metering
20 via a pump, within 3.5 hours. 2.5 and 5 hours after the
feed has finished, 2.34 g of tert.-butylper-2-
ethylhexanoate is added and the mixture is maintained at
95°C for a further 12 hours. The mixture is then
diluted with 497.2 g of 100 N-oil. The actual viscosity
25 is determined at KV100 = 77.6 cSt. The molecular weight
is determined by SEC, $M_w = 19,000$ g/mol.

b) Transesterification

30 A mixture of 1,760.4 g of the product from a), 1,260 g
of methyl methacrylate, 0.06 g of 4-hydroxy-2,2,6,6-
tetramethylpiperidin-1-oxide and 0.23 g of hydroquinone
monomethyl ether are introduced to a 6 l three-necked
flask equipped with electric heating mantle, sabre
35 stirrer, internal thermometer, air inlet pipe and packed
column with regulator-controlled steam distributor.
After removal of 118 g of distillate, 1.15 g of lithium
methoxide is added and refluxed until the boiling

temperature decreases to 65 to 68°C. The methanol-rich distillate (65 to 68°C, about 17 g) is then removed until an increase in the boiling temperature to 100°C indicates that the mixture has largely reacted. After
5 distilling off a further 280 g of distillate at 100°C, the preparation mixture is cooled down to ambient temperature and filtered through a Seitz-KS80 filter layer until it is clear. The excess methyl methacrylate is removed on the vacuum rotation evaporator.
10 Yield: 1750 g of oil solution of the macromonomer A-1.

A-2

Preparing a PAMA-macromonomer $M_w = 5500$

15 a) Preparing the primary OH-substituted phase

The same apparatus is used as under A-1 (a). The following is introduced to a 6 l flask; 1,396 g of 100 N-oil, 155.1 g of methacrylates of a mixture of C_{11} - C_{16}
20 alkanols (product DOBANOL 25L) and 4.65 g of 2-mercaptoethanol are heated to 110°C under nitrogen. After adding 1.65 g of tert-butylper-2-ethylhexanoate, a mixture of 2,448.9 g of the same methacrylates, 75.3 g of 2-mercaptoethanol and 24.5 g of tert.-butylper-2-
25 ethylhexanoate are continuously pumped in within 3.5 hours. 45 minutes and 90 minutes after the feed has ended, 5.2 g of initiator is added and the preparation mixture is maintained at 100°C for a further 2 hours. The resultant product exhibits a viscosity of 20.9 cSt
30 at 100°C.
Yield: 4,038 g.
Actual viscosity KV 100 = 20.9 cSt
Molar weight (SEC) = 5,500 g/mol

35 b) The transesterification is carried out (with the same weight ratios of the starting substances) analogously to A-1b), but in a 10 l three-necked flask using the entire product of a).

Yield about 4,000 g of the macromonomer A-2.

A-3

Preparing a PAMA-macromonomer $M_w = 7,720$

5

a) Preparing the primary phase

The same apparatus is used as in Example A-1a). 1,396 g of 100 N-oil, 155.1 g of methacrylates of a mixture of C₁₁-C₁₆-alkanols (product DOBANOL 25L) and 3.10 g of 2-mercaptoethanol are introduced to a 6 l flask and the mixture is heated to 110°C under nitrogen. After adding 1.65 g of tert.-butylper-2-ethylhexanoate (initiator), a mixture of 2,448.9 g of the same methacrylates, 49.0 g of 2-mercaptoethanol and 24.5 g of initiator are continuously pumped in within 3.5 hours. 45 and 90 minutes after the end of the feed 5.2 g of initiator is added, and the preparation mixture is kept at 110°C for a further 12 hours.

15

Actual viscosity KV 100 = 21 cSt

Molar weight (SEC) = 7,720 g/mol

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b) Transesterification analogous to Example A-2b), yield about 4,000 g of oil solution of the macromonomer

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A-4

Preparing a PAMA-macromonomer $M_w = 13,600$

a) Preparing the primary phase

30

The same apparatus is used as for Example A-1a). 1,396 g of 100 N-oil, 155.1 g of methacrylates of a mixture of C₁₁-C₁₆-alkanols (product DOBANOL 25L) as well as 1.55 g of 2-mercaptoethanol are introduced to a 6 l flask, and the mixture is heated to 110°C under nitrogen. After adding 1.65 g tert-butylper-2-ethylhexanoate, a mixture of 2,448.9 g of the above methacrylates, 25.5 g of 2-mercaptoethanol and 24.5 g of

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tert.-butylper-2-ethylhexanoate are continuously pumped in within 3.5 hours. 45 and 90 minutes after the end of the feed 5.2 g of tert.-butylper-2-ethylhexanoate are added, and the preparation mixture is maintained at
5 110°C for a further 12 hours.

Actual viscosity KV 100 = 52 cSt.

Molar weight (SEC) = 13,600 g/ml.

b) The transesterification is carried out analogously to
10 Example A-2b). Yield about 4,500 g of oil solution of the macromonomer A-4.

Preparing the graft polymer PFP from the macromonomers

15 PFP-1

Preparing a high molecular weight comb polymer

An apparatus according to Example A-1a) is used. The monomer mixture is prepared from 227.7 g of macromonomer
20 of Example A-1, 106.3 g of methacrylates of a mixture of C₁₁-C₁₆-alkanols (product DOBANOL 25 L) and 45.5 g of methyl methacrylate. 24.5 g of this monomer mixture is introduced with 220.5 g of 100 N-oil to the apparatus and heated to 82°C under nitrogen. After adding 0.88 g
25 of tert.-butylper-2-ethylhexanoate to the preparation mixture, 355 g of monomer mixture is continuously pumped in together with 0.56 g of tert.-butylper-2-ethylhexanoate within 3.5 hours. 12 hours after the end of the feed, a further 0.5 g of tert.-butylper-2-
30 hexanoate is added and reacted at 82°C for 8 hours. The mixture is then diluted by adding 150 g of 100 N-oil. Yield: 600 g of oil solution of the graft polymer PFP-1.

PFP-2

35 Preparing a dispersively active comb polymer

The apparatus according to Example A-1a is used).

122.9 g of the macromonomer of Example A-2, 20.0 g of 2-

(N-morpholinyl)-ethylmethacrylate and 0.15 g of dodecylmercaptan are introduced to a three-necked flask, and the mixture is heated to 100°C under nitrogen.

1.0 g of tert.-butylper-2-ethylhexanoate is then added.

5 After 3 or 7 hours of adding the first initiator, a further 0.2 g of tert.-butylper-2-ethylhexanoate is added, and the preparation mixture is maintained at 100°C for a further 12 hours.

Yield: 143 g of oil solution of the comb polymer PFP-2.

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PFP-3

Preparing a dispersively active comb polymer

Apparatus as in Example A-1. 122.9 g of the
15 macromonomers of Example A-3, 20 g of 2-(N-morpholinyl)-ethylmethacrylate and 0.15 g of dodecylmercaptan are introduced to a three-necked flask, the mixture is heated to 100°C, and 1.0 g of tert.-butylper-2-ethylhexanoate is then added. After 3 or 7 hours of
20 adding the first initiator, a further 0.2 g of initiator is added, and the preparation mixture is maintained at 100°C for a further 12 hours.

Yield: 143 g of oil solution of the comb polymer PFP-3.

25 PFP-4

Preparing a dispersively active comb polymer

Apparatus as in Example A-1. 138.2 g of the
30 macromonomer of Example A-4, 10 g of 2-(N-morpholinyl)-ethylmethacrylate (= monomer VII-a) and 0.15 g of dodecylmercaptan are introduced to a three-necked flask, and the mixture is heated to 100°C under nitrogen, and 1.0 g of tert.-butylper-2-ethylhexanoate is then added. After 3 or 7 hours of adding the initiator, a further
35 0.2 g of initiator is added, and the preparation mixture is kept at 100°C for a further 12 hours.

Yield: 148 g of oil solution of the comb polymer PFP-4.

PFP-5

Preparing a dispersively active comb polymer

- Apparatus as in Example A-1. 138.2 g of the
5 macromonomer according to Example A-2, 5.0 g of 2-(N-morpholinyl)-ethylmethacrylate, 5.0 g of N-vinyl pyrrolidone (= monomer VIII-a) and 0.15 g of dodecylmercaptan are introduced to a three-necked flask, and the mixture is heated to 100°C under nitrogen, and
10 1.0 g of tert.-butylper-2-ethylhexanoate is then added. Within 3 or 7 hours of adding the first initiator, a further 0.2 g of tert.-butylper-2-ethylhexanoate is added, and the preparation mixture is kept at 100°C for a further 12 hours.
15 Yield: 148 g of oil solution of the comb polymer PFP-5.

PFP-6

Preparing a high molecular weight comb polymer

- 20 An apparatus according to Example A-1a) is used. The monomer mixture is prepared from 299.5 g of macromonomer of Example A-1, 65 g of methacrylates of a mixture of C₁₁ to C₁₆-alkanols (product Dobanol 25 L), 65.0 g of methyl methacrylate and 70.5 g of 100 N-oil. 50 g of this
25 monomer mixture is introduced into an apparatus and heated to 90°C under nitrogen. After adding 0.06 g of tert.-butylper-2-ethylhexanoate to the preparation mixture, 450 g of the monomer mixture is continuously pumped in together with 0.59 g of tert.-butylper-2-ethylhexanoate within 3.5 hours. 1.5 hours after the
30 feed has ended, 312.5 g of 100 N-oil is added for dilution. 6 hours after the end of the feed, a further 0.65 g of tert.-butylper-2-ethylhexanoate is added and reacted for 8 hours.
35 Yield: 812 g of oil solution of the graft copolymer PFP-6.

PFP-7

Preparing a high molecular weight comb polymer

5 An apparatus according to Example A-1a) is used. The monomer mixture is prepared from 276.5 g of macromonomer of Example A-1, 120.0 g of n-butylmethacrylate and 103.5 g of 100 N-oil. 75 g of this monomer mixture is introduced to the apparatus, and the mixture is heated to 90°C under nitrogen. After adding 0.09 g of tert.-
10 butylper-2-ethylhexanoate to the preparation mixture, 425 g of the monomer mixture is continuously pumped in together with 0.51 g of tert.-butylper-2-ethylhexanoate, within 3.5 hours. 6 hours after the end of the feed, a further 0.6 g of tert.-butylper-2-ethylhexanoate is
15 added, and the mixture is reacted for 8 hours. It is then diluted by adding 100 g of 100 N-oil.
Yield: 600 g of oil solution of the graft copolymer PFP-7.

20 PFP-8

Preparing a high molecular weight comb polymer

25 An apparatus according to Example A-1a) is used. The monomer mixture is prepared from 207.4 g of macromonomer of Example A-1, 165.0 g of n-butylmethacrylate and 127.6 g of 100 N-oil. 75 g of this monomer mixture is introduced to an apparatus, and the mixture is heated to 85°C under nitrogen. After adding 0.09 g of tert.-
30 butylper-2-ethylhexanoate to the preparation mixture, 425 g of the monomer mixture is continuously pumped in together with 0.51 g of tert.-butylper-2-ethylhexanoate, within 3.5 hours. 1.5 hours after the feed has finished, 250 g of 100 N-oil is added to dilute the mixture. 6 hours after the feed has finished, a further
35 0.6 g of tert.-butylper-2-ethylhexanoate is added, and the mixture is reacted for 8 hours. For further dilution 450 g of 100 N-oil is then added.
Yield: 1,200 g of oil solution of the graft copolymer

PFP-8.

Tests

5 In order to test the emulsifying action of the graft polymers according to the invention, the following toluene/water emulsification test may be used. In order to test their dispersion action, the carbon spot test may be used.

10

Carrying out the toluene/water emulsification test:
The additive to be tested for its emulsifying action is dissolved in toluene (mixed with 20 ppm Oracet blue B) with the polymer concentration of 1 wt.-%. 7 ml of
15 distilled water and 13 ml of the 1% toluene solution are successively introduced into a graduated 20 ml ground test glass and tempered at 30°C in the water bath, for 15 minutes. By vigorously shaking the test glass a uniform emulsion is produced and the sample is put back
20 into the tempering bath. The separation of the emulsion into the layers of toluene, emulsion and water is observed over a period of 24 hours. For this, the toluene/emulsion layer boundary and the emulsion/water layer boundary is read on the graduated scale (see
25 Figure 1a) after 5 minutes, 10 minutes, 100 minutes and 24 hours.

Evaluation

30 The quantification of the emulsifying action in percentage values is carried out according to diagram 1b. Here, the proportion of the emulsion present during the time of observation of 5 minutes to 24 hours is characterised by the ratio between area A and the total
35 area A + B and determined in percentages.

Carrying out the carbon spot test:

Two stock solutions (stock solution I containing 0.375% of polymer and stock solution II containing 0.75% of polymer) are mixed with the additive to be tested in 150 N-oil (Enerpar 11). Two carbon dispersion solutions are prepared from each stock solution (repeated test). For this, 1.5 g of carbon (furnace black, Degussa special black 4) and 50 g of stock solution are each weighed into a 150 ml beaker and stirred by means of an Ultra-Turrax intensive stirrer for 30 minutes at 9,000 rev/min. 20 μ l of each dispersion solution is then put in the form of spots on filter paper (Papier Durieux 122). After flat storage for 48 hours at 30°C, the spots are evaluated. For this, the diameter of the carbon spot and the diameter of the surrounding oil spot are measured and their ratio is given in percentage.

Individual evaluation:

Diameter carbon spot/diameter oil spot * 100 %.

The total value of the spot test is derived from the sum of the four individual percentage values. Products with a poor carbon dispersion produce total values of about 70% and less, products with a good carbon dispersion produce total values of $\geq$ 130%.

Comparing the rheological characteristics of the copolymers PFP-1, PFP-6, PFP-7 and PFP-8 with those of a commercially available PAMA-VI improving agent, VISCOPLEX 8-500 made by Röhm GmbH

TABLE 1

Additive	Formulation in 150 N-measuring oil		Capillary viscosimetry			Shearing stability	
	wt.-% Additive	= % Polymer	100°C (cSt)	40°C (cSt)	VIB	% decrease KV 100	ASTM D 2603 Ref B PSSI
PFP-1	12.5	5.0	12.32	61.37	203	26.7	48.1
PFP-6	12.5	5.0	12.90	60.49	219	32.4	56.3
PFP-7	10.0	5.0	12.55	53.72	241	25.5	45.5
PFP-8	20.0	5.0	12.71	44.51	297	16.4	29.0
VISCOPLEX 8-500	9.9	5.0	12.87	70.0	187	26.0	45.3

As is apparent from Table 1, the PAMA-copolymers exhibit clearly higher viscosity index values with a comparable thickening action (KV 100) and a comparable shearing stability.

TABLE 2

Formulation in
150 N-measuring oil
with 0.3% of PPD *)

Capillary viscosimetry

Additive	wt.-%	= % Polymer	100°C (cSt)	40°C (cSt)	0°C (cSt)	-10°C (cSt)	-20°C (cSt)
PFP-1	14.45	5.78	14.08	69.29	783.6	1 714	4 683
PFP-6	13.75	5.50	14.23	65.65	636.1	1 503	4 395
PFP-7	11.20	5.60	13.91	58.47	573.3	1 287	3 814
PFP-8	22.0	5.50	14.05	47.75	464.9	1 071	2 936
VISCOPLEX 8-500	10.05	5.53	14.06	75.72	869.5	1 891	5 635

*) PPD = pour point improving agent VISCOPLEX 1-330

The comparison of the formulations in Table 2, which have been set to the same viscosity at 100°C, also show that there is clearly less thickening of the copolymers at lower temperatures.

Characterisation of the dispersively active copolymers and the activity thereof:

TABLE 3

Additive	Viscosity data in 150 N-measuring oil					Dispersion evaluation			
	Description (wt.-%)	Composition	% Polymer	% Additive	KV 100 (cSt)	KV 40 (cSt)	VIB (cSt)	TW test	Carbon spot test
PFP-2	Macromonomer A-2/ Monomer VII-a (80 - 20)	70	11.43	8.39	48.8	148	17 %	130 %	
PFP-3	Macromonomer A-3/ Monomer VII-a (80 - 20)	70	11.43	8.07	47.8	141	21 %	145 %	
PFP-4	Macromonomer A-4/ Monomer VII-a (90 - 10)	67.5	11.85	8.69	52.4	143	11 %	156 %	
PFP-5	Macromonomer A-1 Monomer VII-a + Monomer VIII-a (90 - 5 - 5)	67.5	11.85	10.21	61.2	155	36 %	132 %	

The PAMA-copolymers listed in Table 3 show a high activity both in the T/W test and in the carbon spot test. Comparable linear PAMA-copolymers having the same growth composition show a high value in the carbon spot test, but no boundary activity in the T/W test.

Toluene/water dispersion test

Fig. 1a: Method

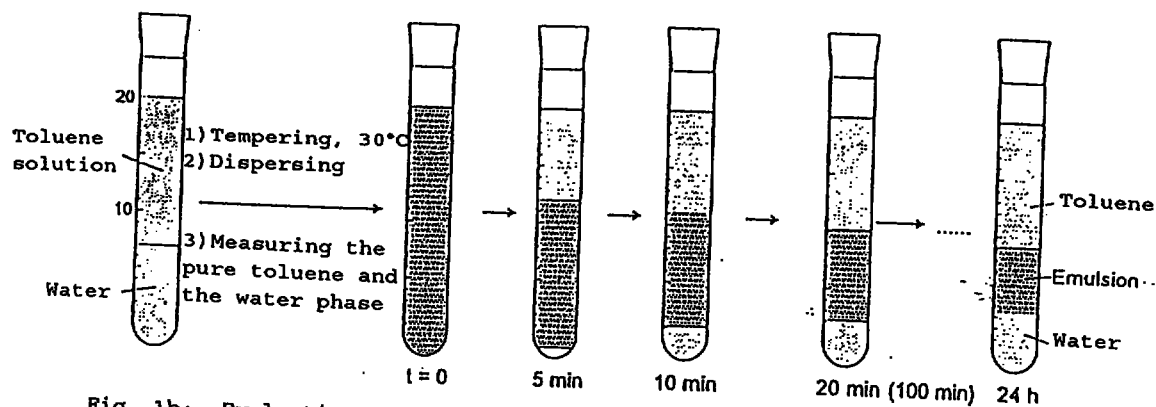
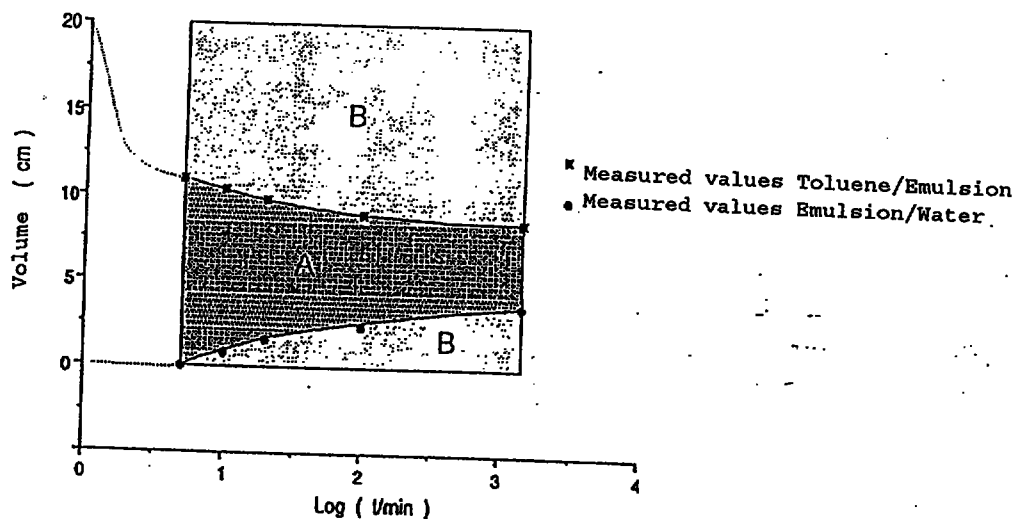


Fig. 1b: Evaluation



Emulsifying action
(area %)

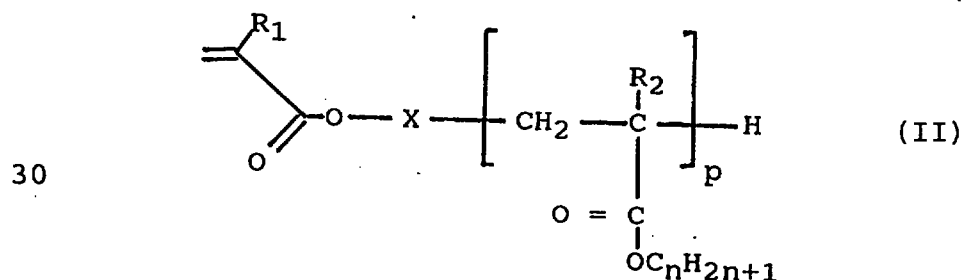
$$= \frac{\text{Area A}}{\text{Area (A + B)}} \cdot 100$$



CLAIMS

1. Lubricating oil additives comprising a graft polymer with a viscosity index-improving activity, wherein said graft polymers PFP are synthesised, in amounts of 10 - 90 wt.-% based on PFP, from polyalkylmethacrylate macromonomers (A) which are copolymerised with 10 - 90 wt.-% based on PFP of alkyl(meth)acrylic acid esters (AMA) having C₆-C₃₀-alkyl groups and with 0 - 60 wt.-% based on PFP of non-functionalised comonomers (B) selected from the group comprising alkyl(meth)acrylic acid esters having C₁-C₅-alkyl groups, styrene, alkyl styrenes having C₁-C₄-alkyl groups and fatty acid vinyl esters having 2 to 12 carbon atoms in the fatty acid group and with 0 - 40 wt.-% based on PFP of functionalised comonomers (C) selected from the group comprising functionalised (meth)acrylates, (meth)acryl amides and vinyl heterocycles, with the proviso that the sum of the copolymerised monomers (AMA) + (B) + (C) based on PFP adds up to 10 to 90 wt.-%, in a carrier medium TM.

2. Lubricating oil additives according to claim 1, wherein the polyalkylmethacrylate macromonomers (A) are compounds of formula II



wherein

X denotes a bivalent group,

R₁ denotes -H or -CH₃,

R₂ denotes -H or -CH₃,



$n = 6$ to 30 , and

p = average polymerisation degree of the macromonomer

5 with the proviso that the average molecular weight M_w of the macromonomer of formula II is within the region 1000 to $100,000$.

10 3. Lubricating oil additives according to claims 1 and 2, wherein the average molecular weight of the graft polymers PFP is within the range 5000 to $1,000,000$.

15 4. Graft polymers PFP' synthesised from $10 - 90$ wt.-% of multi-functionalised polyalkylmethacrylate macromonomers (A') comprising

0 - 90 wt.-% of alkyl(meth)acrylic esters (AMA') having C_6-C_{30} -alkyl groups,

20 0 - 40 wt.-% of non-functionalised comonomers (B') from the group comprising alkyl(meth)acrylic acid esters having C_1-C_5 -alkyl groups, styrene, alkyl styrenes having C_1-C_4 -alkyl groups and fatty acid vinyl esters having 2 to 12 carbon atoms in the fatty acid group, and

25 0 - 100 wt.-% of functionalised comonomers (C') selected from the group comprising functionalised (meth)acrylates, (meth)acrylamides and vinyl heterocycles,

30 with the proviso that the sum of the monomers (AMA'), (B') and (C') in the macromonomer (A') adds up to 100 wt.-%,

35 said macromonomer (A') being copolymerised with

0 to 90 wt.-% of monomers selected from the group comprising alkyl(meth)acrylic acid esters (AMA) having C_6-C_{30} -alkyl groups,



0 to 60 wt.-% of monomers (B) selected from the group comprising alkyl(meth)acrylic acid esters having C₁-C₅-alkyl groups, styrene, alkyl styrenes having C₁-C₄-alkyl groups and fatty acid vinyl esters having 2 to 12 carbon atoms in the fatty acid group, and

0 to 40 wt.-% of functionalised comonomers (C) selected from the group comprising functionalised (meth)acrylates, (meth)acrylamides and vinyl heterocycles,

with the proviso that the sum of copolymerised monomers (AMA), (B) and (C) is 10 to 90 wt.-% based on PFP'.

5. Lubricating oil additives according to claim 1 comprising the graft polymers PFP' according to claim 4 as graft polymers.

GRAFT POLYMERS AND THEIR USE AS LUBRICANT ADDITIVES

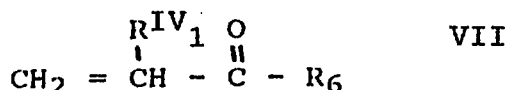
ABSTRACT

The invention relates to lubricating oil additives comprising graft polymers with a viscosity index-
5 improving action, the graft polymers PFP being synthesised from 10 - 90 wt.-% based on PFP of polyalkylmethacrylate macromonomers (A) which are copolymerised with 0 - 90 wt.-% based on PFP of
10 alkyl(meth)acrylic acid esters (AMA) having C₆-C₃₀-alkyl groups, and with 0 - 60 wt.-% based on PFP of non-functionalised comonomers (B) selected from the group comprising alkyl(meth)acrylic acid esters having
15 C₁-C₅-alkyl groups, styrene, alkyl styrenes having C₁-C₄-alkyl groups and fatty acid vinyl esters having 2 to 12 carbon atoms in the fatty acid group, and with
0 - 40 wt.-% based on PFP of functionalised comonomers (C) selected from the group comprising functionalised
20 (meth)acrylic acid esters and amides and vinyl heterocycles with the proviso that the sum of the copolymerised monomers based on PFP is 10 to 90 wt.-%, in a carrier medium TM.

REPLACEMENT SHEET

18 JUN 1996

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wherein R^{IV}_1 denotes hydrogen or methyl, R_6 denotes $-\text{OR}_9$ or $-\text{NR}_7\text{R}_8$ and wherein R_9 denotes an alkyl group having 2 to 20 carbon atoms which is substituted by at least one hydrophilic group A selected from the group comprising hydroxyl, an $-\text{NR}'_7\text{R}'_8$ group, a sulphonic acid group, a carboxyl or carboxamide group or a 5 to 6-membered heterocycle which is itself soluble in water, in which the carbon chain may be interrupted by ether bridges or terminated by a phenyl or phenoxy group optionally substituted by a $\text{C}_1\text{-C}_{12}$ -alkyl group, and wherein R_7 , R_8 , R'_7 and R'_8 may be hydrogen or an alkyl group having 1 to 6 carbon atoms which may optionally be substituted by a hydrophilic group A, or wherein R_7 , R_8 , R'_7 and R'_8 , optionally together with further nitrogen or oxygen atoms, may form a 5- or 6-membered heterocycle, and wherein R_7 , R_8 , R'_7 and R'_8 may be hydrogen or an alkyl group having 1 to 6 carbon atoms, whilst $-\text{NR}'_7\text{R}'_8$ may optionally be quaternised, or if R_7 is hydrogen, R_8 may also be a carboxamido group.

Preferably, the functionalised comonomers (C) are selected from the group comprising optionally substituted (meth)acrylamide, hydroxy alkyl esters of (meth)acrylic acid such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, amine-substituted alkyl esters such as 2-diethylaminoethyl(meth)acrylate, 2-(1-imidazolyl)ethyl(meth)acrylate, 2-(4-morpholinyl)ethyl(meth)acrylate, 2-trimethylammoniummethyl(meth)acrylate salts, hydroxalkyl substituted (meth)acrylamides such as N-(2-hydroxyethyl)(meth)acrylamide, N-(3-hydroxy-2,2-dimethylpropyl)(meth)acrylamide, N-dimethylaminomethyl(meth)acrylamide, N-(meth)acryloidpyrrolidon-2-(meth)acrylamide, N-(meth)acrylamidomethylpyrrolidone, N-(1-piperidinylmethyl)-(meth)acrylamide, quaternary ammonium