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## Description

## 5 Area of the invention

The invention relates to a process for preparing homo- and cooligomers, especially cooligomers of (meth)acrylic acid esters and  $\alpha$ -olefins which may be used as synthesis  
10 oils or components of such oils, as mineral oil additives as well as plastifiers and the like.

## Prior art

15 In general, oligomers are compounds with a molecular weight of from  $10^2$  -  $10^5$ , especially  $10^2$  -  $10^4$ , which are synthesised from corresponding monomer units. (cf. Römpp's Chemie-Lexikon, 8th Ed., p. 2893, Franckh'sche  
20 Verlagsbuchh. 1985). Prior art examples, on which this invention is based, include cooligomers of (meth)acrylic acid esters and  $\alpha$ -olefins. Oligomers of acrylic acid esters, as understood nowadays, are disclosed, for example, in C.E. Rehberg et al. in Ind. Eng. Chem. 44  
(12) 2864, 1952).

25

US-A 3 968 148 or DE-A 22 43 064 describe, for example, this type of oligomer which are synthesised from three monomer groups. These oligomers comprise:  
about 10 - 90 wt.% of an 1-alkene having 4 to 32 C-atoms  
30 about 1 - 35 wt.% of one or more alkyl(meth)acrylic acid esters having 8 to 34 C-atoms in the alkyl group and  
about 1 - 35 wt.% of one or more alkyl esters of  
(meth)acrylic acid or homologous,  
35 terminally unsaturated carboxylic acids having 1 to 4 C-atoms in the alkyl group.

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Oligomers of this kind preferably have a molecular weight of  $M_n = 1,000$  to  $4,000$ . Mention must be made of the narrow molecular weight range and of the high uniformity of the products. US-A 4 009 195 also  
5 discloses an oligomerisation process, in which various (meth)acrylic acid derivatives such as C1-C4-alkyl esters in amounts of 1 to 35 wt.% and (meth)acrylic acid esters of C8-C34-alkanols in amounts of 1 to 45 wt.%,  
10 are continuously and simultaneously added to a mixture of radical initiators and 10 to 90 wt.% of a 1-alkene having 4 to 32 C-atoms, so that the molar ratio, which arises more or less immediately, between acid derivatives and 1-alkene is kept relatively constant in the reaction preparation within a range of 0.001 to 0.2.  
15 The addition, here, should be at a temperature which does not affect oligomerisation. The yields are given as 40 to 70%, the residue, in particular, being  $\alpha$ -olefin.

20 Furthermore, DE-A 32 23 694 discloses copolymers of  $\alpha$ - $\beta$ -unsaturated dicarboxylic acid esters with  $\alpha$ -olefins. By definition, the  $\alpha$ - $\beta$ -unsaturated dicarboxylic acid esters contain, as alcohol component, straight-chained or branched monoalcohols having 3 to 10 carbon atoms;  
25 the  $\alpha$ -olefins have 10 to 16 carbon atoms. The copolymers, may, optionally, be crosslinked and their pour-point must be between  $-60$  and  $0^\circ\text{C}$ .

US-A 4 526 950 discloses a method for preparing  
30 copolymers, in which the mixture of the components, based on at least one  $\alpha$ -olefin having at least 6 C-atoms, and at least one unsaturated carboxylic acid or derivatives copolymerisable with olefins, is heated to at least  $135^\circ\text{C}$  in the presence of a radical initiator  
35 and in the absence of solvents or diluents. Here, none of the reactive monomers is used in excess in order to avoid a dilution of activity. SU-A 1 135 752 also discloses copolymers comprising decyl methacrylate and

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tetradecene with a molar weight of 8,000 to 13,000, which are used as thickening agents in lubricating oil.

5 EP-A 217 602 describes oil additives based on ethylene copolymers which comprise inter alia ethylenically unsaturated mono- or dicarboxylic acids and the esters thereof which have a molar weight of  $M_n < 1,000$ .

#### Object and solution

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One method for reducing the molecular weight in the radical polymerisation of monomers is the use of regulators, especially mercaptans (cf. G. Henrici-Olivé et al. Fortschr. Hochpolym. Forsch. Vol. 2., p. 496 - 15 577 (1961); Houben-Weyl, Methoden der Organ. Chemie, 4th ed., vol. XIV/I).

A further suitable method described in the literature is the overdosing of catalyst. This, however, makes the 20 process more expensive. Furthermore, experiments have been carried out for obtaining oligomers of methyl methacrylate during heating in the liquid phase above 160°C, in the presence of an inhibitor. Experience shows that an increase in temperature and in pressure 25 and longer reaction times promote the formation of higher oligomers. (Houben-Weyl, 4th ed., vol. XIV/I p. 1046, 1072 - 1073, Georg-Thieme-Verlag 1961).

However, process conditions which are too drastic should 30 not be used for a technical process which is, moreover, based on the exothermic radical polymerisation. Yet, if the prior art preparation of oligomers or cooligomers comprising (meth)acrylic acid esters and  $\alpha$ -olefins, is used, for example, the lack of generally applicable 35 process rules which ensure constant success is apparent. The processes shown were also not able to fully satisfy the requirements in individual cases. The prior art application of (meth)acrylate oligomers is characterised



by:

- 5       - the apparatus used, in particular for the anionic polymerisation, is necessarily expensive, since the operation takes place under inert conditions; relatively pure monomers are needed; use of a solvent is standard procedure.
- 10       - when regulators are used in radical reactions, commonly known problems occur with the incorporation of terminal groups as, for example, in the case of mercaptans.
- 15       - furthermore, high concentrations of initiator are used. Apart from the considerable costs involved, it also means a greater safety risk.

20       It has now been found that the process of this invention makes cooligomers, especially those of (meth)acrylic acid and  $\alpha$ -olefins significantly more accessible.

25       This invention relates to a process which makes it possible to homopolymerise (meth)acrylates or copolymerise them with further monomers and in which the molecular weights may be adjusted over a wide range which covers the entire oligomer range and even extends beyond it. No regulator is used here. The amount of initiator used is normally not greater than the amount usually needed for solution polymerisations. The

30       molecular weight adjustment to obtain lower molecular weights, in particular, is not predominantly effected by varying the amount of initiator used, as is disclosed in the prior art.

35       The systems described comprise a component B), which has a higher polymerisation tendency (such as (meth)acrylates), plus a component A), which has a lower polymerisation tendency, and/or a suitable solvent L.



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The molecular weight of the oligomers, right down to the lower molecular oligomers including dimers/trimers, is regulated via the following variables:

- 5      $\alpha$ )   The ratio of B) to A) or to A) plus L or to L alone. Under otherwise similar conditions, with a larger amount of A) and/or L or A) alone, lower molecular weights are obtained.
- 10     $\beta$ )   The feed time for B). If the feed times are increased, lower molecular weights are obtained under the same conditions.
- 15      $\gamma$ )   The reaction temperature which is selected within a range in which a conventionally prepared, regulator-free homopolymer of the more polymerisable component B) depolymerises to a noticeable degree. This means that at the chosen temperature, in the monomer/polymer equilibrium,
- 20     there are already larger amounts of monomer, normally 3 to 80 wt.%, especially 10 to 60 wt.%. Thus, depending on the required molecular weight range for n-decyl methacrylate, for example, a suitable temperature range is from 120°C to 170°C,
- 25     in which between 3 and 80 wt.% of the monomers are in equilibrium. A temperature, at which there are between 15% and 50% of monomers (here 140 to 160°C) is particularly suitable for molecular weights  $\bar{M}_w$  in the lower molecular weight range with
- 30     simultaneously high yield. In this way, depending on the chosen reaction temperature, the formation of long B) sequences may be suppressed to a greater or lesser extent which means that in addition to  $\alpha$ ) and  $\beta$ ) the molecular weight may be effectively
- 35     controlled by lowering the reaction temperature in the above range, the molecular weights of the (co)oligomers thereby being increased.



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By varying  $\alpha$ ),  $\beta$ ) and  $\gamma$ ) it is possible to adjust the molecular weights of about 500 to 100,000 in a simple and reproducible manner without using regulators. Through a correct choice of the parameters, including  
5 the total reaction time, a complete reaction of the monomers may also be achieved easily. Thus, the process according to the invention has the further advantage that the residual monomers do not have to be separated (see Examples). If the formulation is such that apart  
10 from A) no further "solvent" is used and A) is completely reacted which is easily possible (see Examples), a further working up of the preparation mixture may be dispensed with. If in formulations with  
15 an inert solvent, a solvent L is chosen which may remain in the product such as PAO or mineral oil for which oligomers are used as the synthetic component of the base oil, or previously prepared oligomer is used as solvent for preparing further oligomer, the separation  
20 of the solvent may also be dispensed with (Examples 10 and 13).

Thus, this invention relates to a process for preparing oligomers and cooligomers through radical polymerisation with at least one monomer component B) with a higher  
25 polymerisation tendency and 0 to 90 wt.%, preferably 1 to 50 wt.% (based on the oligomers) of a monomer component A) with a lower polymerisation tendency, at an elevated temperature and in the presence of polymerisation initiators in a conventional  
30 polymerisation vessel, whereby:

- a) a liquid phase comprising the monomer component A) or a solvent L or both is introduced into the polymerisation vessel and heated to the reaction  
35 temperature.
- b) the component B) with a higher polymerisation tendency is added after the component A) has been



introduced, so that the molar ratio between the components B) and A) passes through values of from 0 to about 0.2 in the initial phase of the polymerisation and achieves the value of 0.2 to 20 in the end phase of the polymerisation, with the proviso that

- 5
- c) the reaction temperature is chosen within a range in which there is already a significant depolymerisation of the homopolymer (prepared without regulator) comprising the monomer component B) which has better polymerisation characteristics. In order to determine a "significant depolymerisation" please note that under these
- 10
- 15 temperature conditions there are already larger amounts of monomers, normally 3 to 80 wt.%, in particular 10 to 60 wt.%, especially 15 to 50 wt.% (based on the sum of the monomers plus polymer) in the monomer/polymer equilibrium,
- 20
- d) the initiator I is added throughout the entire polymerisation, the initiator I being selected such that the half life at the corresponding reaction temperature is one minute to about five hours and
- 25
- the amount of initiator used is 0.1 to 10, preferably 1 to 5 wt.% based on the total amount of monomers.

Normally, the skilled man has sufficient know-how from the prior art literature (e.g. K Wachstum)

K Abbruch

in order to differentiate between monomers with a high radical polymerisation tendency B) or C) and those with a lower polymerisation tendency (Monomer A). One way of assessing the relevant polymerisation tendency is, for example, the use of the widely differing Q-values of the monomers (according to Alfrey-Price, cf. Brandrup-Immergut Polymer Handbook loc.cit. II/267). Generally,



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it may be assumed that the monomers have either a higher or lower polymerisation tendency, if the two numerical values of Q differ from each other by a factor  $\geq 5$ . 1-Hexene as monomer component A) has, for example, a Q-value of 0.035, butyl methacrylate, for example, has the Q-value of 0.82.

According to the invention, the monomer component A), to be used in amounts of 0 to 90 wt.%, preferably comprises at least one radically polymerisable  $\alpha$ -olefin having 4 to 40 carbon atoms, here, the cooligomer composition of CM normally comprises 5 to 90 wt.% of A), the remainder being B) (= cooligomers CM'). Preferably, the component B) comprises at least one acrylic or methacrylic acid ester of Formula (I)



20

wherein R is hydrogen or methyl and  $\text{R}_1$  may be an optionally branched, optionally cyclic alkyl group having 1 to 42 carbon atoms, in which individual chain members may be substituted by ether groups -O-, in which there is a spacing of at least two carbon chain members between the individual ether groups, in which  $\text{R}_1$  may additionally be substituted by one or more functional groups Y which comprise at least one nitrogen or oxygen atom bound to carbon. Preferably, Y is a  $-\text{NR}_2\text{R}_3$ ,  $-\text{OR}_4$ ,  $-\text{COOR}_5$  or  $-\text{C}-\text{CH}-$  group, wherein  $\text{R}_2$  and

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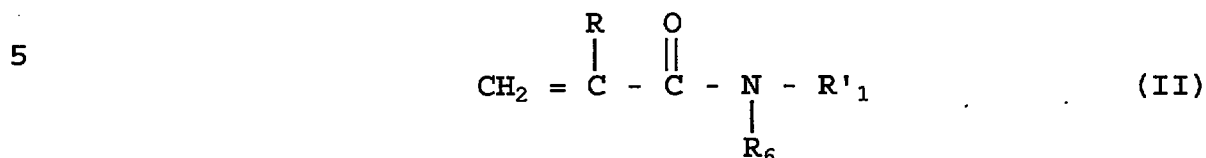
$\text{R}_3$ , independently of each other, are alkyl groups with 1 to 4 carbon atoms, wherein  $\text{R}_2$  and  $\text{R}_3$ , together with the nitrogen and optionally further nitrogen or oxygen atoms may be a 5- or 6-membered ring, and wherein  $\text{R}_4$  and  $\text{R}_5$  are hydrogen or an alkyl or cycloalkyl group with 1 to 40, preferably 1 to 10, carbon atoms. If cycloalkyl groups are present, they are preferably 5- to 8-membered ring

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systems. Furthermore, the component B) may comprise monomers of Formula II

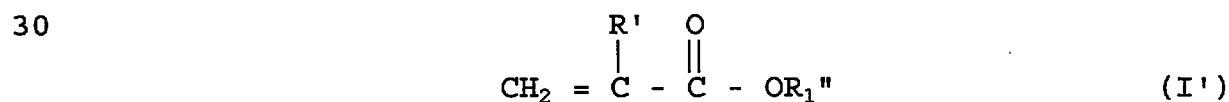


10 wherein R' and R'<sub>1</sub> have the meanings of R or R<sub>1</sub> and R<sub>6</sub> is hydrogen or has the same meaning as R<sub>1</sub>.

According to the invention, the process is particularly preferred for preparing homo-oligomers from the monomer component B), particularly (meth)acrylic acid esters of  
15 Formula (I) (see above), especially from the monomers B') (see below), more particularly from B'-α.  
Furthermore, the process according to the invention is preferably used for preparing cooligomers CM",  
20 synthesised from

A) 0 to 75 wt.%, preferably 10 to 40 wt.% of at least an 1-alkene having 4 to 32 carbon atoms, preferably 10 to 14 carbon atoms in the molecule  
25 and

B'-α) 20 to 100 wt.%, preferably 40 to 90 wt.% of at least one (meth)acrylic acid ester of Formula I'



wherein R' is hydrogen or methyl and R<sub>1</sub>" is an optionally branched alkyl group or a cycloalkyl group having 4 to 32 carbon atoms, preferably 8 to 20 carbon atoms in the alkyl group and  
35

B'-β) 0 to 65 wt.%, preferably 0.5 to 50, more particularly 3 to 40 wt.%, of a (meth)acrylic acid ester of Formula I"  
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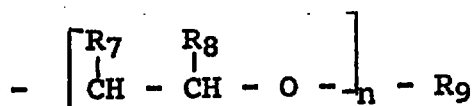


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5 wherein R' is hydrogen or methyl and R<sub>1</sub>'' is an alkyl group with 2 to 6 carbon atoms, substituted with at least one group Y', wherein Y' has the same meaning as Y, more particularly substituted with a hydroxyl group, or R<sub>1</sub>'' is a group

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15

wherein R<sub>7</sub> and R<sub>8</sub> are hydrogen or methyl, R<sub>9</sub> is hydrogen or an optionally branched alkyl group with 1 to 40, preferably 1 to 20 carbon atoms, and n is an integer from 1 to 60, with the proviso that if n is 1, R<sub>8</sub> is at the same time only an optionally branched alkyl group having 1 to 40 carbon atoms.

20

The components A') and B') of the cooligomers normally make up 100 wt.%. Examples of the monomer component A) include:

25

butene-1, pentene-1, hexane-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadene-1, octadecene-1, nonadecene-1, eicosene-1, heneicosene-1, 30 docosene-1-, ttricosene-1, tetracosene-1, pentacosene-1, hexacosene-1, heptacosene-1, octacosene-1, nonacosene-1, triacontene-1, hentriacontene-1, dotriacontene-1, or the like. Suitable monomer components also include branched alkenes such as vinylcyclohexane, 3,3-dimethylbutene-1, 35 3-methylbutene-1, diisobutylene-4-methylpentene-1 or the like. 1-Alkenes with 10 to 32 carbon atoms, which are obtained during the polymerisation of ethylene, propylene or mixtures thereof, are also suitable. These materials, themselves, are obtained from hydrocracked



substances.

The variant in which component A) of the cooligomers CM is 1-decene or dodecene, tetradecene is particularly preferred. Also of special interest are oligomers or cooligomers CM wherein component B) comprises (meth)acrylic acid esters having 4 to 22 carbon atoms in the (branched or unbranched) alkyl group, or mixtures thereof.

10

Examples of monomers include e.g.:

butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, isodecyl acrylate, decyl acrylate, undecyl acrylate, dodecyl acrylate, tridecyl acrylate, tetradecyl acrylate, pentadecyl acrylate, hexadecyl acrylate, heptadecyl acrylate, octadecyl acrylate, cetylstearyl acrylate, oleyl acrylate, nonadecyl acrylate, eicosyl acrylate, cetyleicosyl acrylate, stearyleicosyl acrylate, docosyl acrylate, eicosyltetratriacontyl acrylate or the corresponding methacrylates. Special mention must be made alkyl methacrylates with  $\geq C_{10}$  in the alkyl group which have a higher iso content. These include, for example,  $C_{12}$ - $C_{15}$ -alkylesters of methacrylic acid with an iso content of about 60 to 90%, as well as isodecyl methacrylate. For certain applications it is also possible to use monomers according to Formula I, wherein  $R_1$  is  $C_1$ - $C_3$ -alkyl, in particular methyl methacrylate in addition to ethyl acrylate, ethyl methacrylate, propyl acrylate and propyl methacrylate. Here, however, the lower boiling points have a limiting effect on the reaction at normal pressure.

35 Examples of the monomer group B) of Formula I also include the following amino-substituted alkyl esters of (meth)acrylic acid:



- 2-diaminomethyl (meth)acrylate,  
2-diethylaminoethyl (meth)acrylate,  
3-dimethylamino-2,2-dimethylpropyl-1- (meth)acrylate,  
3-dimethylamino-2,2-dimethylpropyl-1- (meth)acrylate,  
5 2-morpholinoethyl (meth)acrylate,  
2-tert.-butylaminoethyl (meth)acrylate,  
3- (dimethylamino)propyl (meth)acrylate,  
2- (dimethylaminoethoxy-ethyl) (meth)acrylate.
- 10 Mention must also be made of the following oxy- or  
alkoxy-substituted alkyl esters of (meth)acrylic acid :  
2-hydroxyethyl (meth)acrylate,  
2-hydroxypropyl (meth)acrylate,  
2-methoxyethyl (meth)acrylate,  
15 2-ethoxyethyl (meth)acrylate,  
2-butoxyethyl (meth)acrylate,  
2- (2-butoxyethoxy)ethyl methacrylate,  
2- (ethoxyethyloxy)ethyl (meth)acrylate,  
4-hydroxybutyl (meth)acrylate,  
20 2- [2- (2-ethoxyethoxy)ethoxy]ethyl (meth)acrylate,  
3-methoxybutyl-1- (meth)acrylate,  
2-alkoxy-methylethyl (meth)acrylate,  
2-hexoxyethyl (meth)acrylate.
- 25 Examples of the monomer group B) of Formula (II) include  
the following (meth)acrylamides:  
N-methyl (meth)acrylamide,  
N-dimethylamino (meth)acrylamide,  
N-dimethylaminopropyl (meth)acrylamide,  
30 N-isopropyl (meth)acrylamide,  
N-tert.butyl (meth)acrylamide,  
N-isobutylmethyl (meth)acrylamide,  
N-decyl (meth)acrylamide, N-cyclohexyl (meth)acrylamide,  
N- [3- (dimethylamino)-2,2-dimethylpropyl]-methacrylamide,  
35 N-dodecyl (meth)acrylamide,  
N- [3-dimethylaminopropyl] (meth)acrylamide,  
N- [2-hydroxyethyl] (meth)acrylamide.



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The solvent L used for the monomers must be stable and inert under the chosen reaction conditions. Generally, in order to avoid any pressure reactions, the boiling point must be above the chosen reaction temperature.

5 Solvents of this kind are known per se.

#### Preparing cooligomors CM

As already stated, the preparation of oligomers or cooligomers from the two monomer classes is known per se, using radical-induced polymerisation e.g. thermal polymerisation and whilst adding a suitable initiator and/or Redox system (cf. prior art). The process of the invention may be used for preparing cooligomers CM which

10 are either new or whose comonomer composition is known. The process according to the invention is noted for its great applicational possibilities and excellent results, but certain process conditions must be maintained.

15 During the process, the monomer component A) with a low polymerisation tendency and/or the solvent L are heated to a reaction temperature in a suitable polymerisation vessel equipped with thermometer, heating and stirring devices. The solvent L must be stable and inert under the reaction conditions. The boiling point is

20 preferably above the chosen reaction temperature. Examples of solvents include aliphatic or aromatic hydrocarbons, such as xylene or cymene, decane or dodecane, but mineral oils, polyalphaolefins, esters and previously prepared oligomers are also suitable as

25 solvents.

30

The use of mineral oils or other non-mineral oil based synthesis oil liquids, is of particular advantage if the cooligomers are intended to be used as base liquids for

35 synthesis oils (cf. Ullmann's Encyclopädie der Techn. Chemie, 4th Ed., Vol. 20, p. 454 - 530, Verlag Chemie 1981), in particular the types later to be used as mixing components. Here, mention must be made of



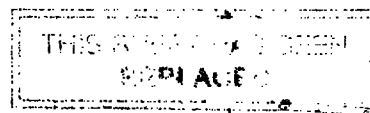
polyalphaolefins of various viscosity classes,  
hydrocrack oils, various ester oils such as TMA-OD-  
esters as well as commercially available mineral oils  
such as of the 100N or 150N-class.

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According to feature C), the reaction temperature is  
chosen within a range in which a homopolymer (prepared  
without regulator) from a monomer component B) which has  
better polymerisation characteristics depolymerises to a  
10 noticeable extent. A "noticeable depolymerisation"  
normally exists when there are already large amounts of  
monomers in the (thermally related) monomer/polymer  
equilibrium. As a guide, there is 3 to 80 wt.% of  
monomer in the equilibrium. However, there are certain  
15 requirements for determining the  
polymerisation/depolymerisation equilibria and no data  
exist as yet in respect of a number of monomers or  
temperature regions. In order to give a rough but  
practical estimate of the temperature range suitable for  
20 the process, the simple method of thermogravimetry has  
proved useful. Here, a conventionally prepared  
homopolymer of the more easily polymerisable component  
B) is examined at increasing temperature, under oxygen  
exclusion using thermogravimetry. In order to carry  
25 out preliminary oligomerisation experiments, the  
temperature range should be considered which starts at  
50°C below the temperature at which the first weight  
losses occur because of depolymerisation, and which ends  
at about 30°C above this temperature.

30

According to the invention, the selection and mode of  
feed of the radical initiators I are also important:  
the initiators I selected must have a half-life at the  
corresponding reaction temperature of from about 1  
35 minute to about 5 hours. (Cf. Kirk-Othmer, 3rd. Ed.  
Vol. 13. pg. 355 - 373, Interscience 1981; Brandrup-  
Immergut, Polymer Handbook loc.cit. II/1).



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The initiators are introduced during the entire polymerisation (with the exception of the final polymerisation which mostly takes 30 minutes to 1 hour). The reaction normally takes about 10 to 15 hours, for example about  $12 \pm 1$  hours. 1/10th up to half of this time, that is, 1 - 5.5 hours is normally taken up by the phase in which the monomer is fed in. The initiators are fed in during the entire reaction, preferably, either in batches at suitable intervals e.g. every half hour, or continuously e.g. by feed mode. The addition of 0.001 - 0.005 mol of initiator each per portion every half hour may be given as a guide (based on each mol of monomers A) or B)). The amount of initiator used is 0.1 to about 10 wt.% based on the total amount of monomers. Suitable initiators are, for example, peroxide initiators, provided they meet the above criteria. They include di-tert.-butylperoxide tert.butylperbenzoate or tert. butylperoctoate, but these are only a few examples.

Based on present findings, according to the invention, a reaction of the monomers of e.g. 98% may be largely achieved by a suitable choice of the reaction conditions, so that in many cases the monomers need not be separated off or indeed further processed. In the remaining cases, the residual monomer comprises almost exclusively component A) which is separated off, depending on the application. The products are inter alia colourless oily liquids which are completely miscible with mineral oil, PAO, HC-oils and ester oils if the content of B'-  $\beta$  does not exceed certain limits e.g. 50 wt.%.

#### Advantageous characteristics

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As already stated in the prior art, the cooligomers CM according to the invention may be used for various technical applications. They are suitable as valuable



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components of synthesis oils. If they comprise functional groups (e.g. according to feature B'-  $\beta$ ), the synthesis oils exhibit dispersing activity.

5 Furthermore, they are used as low-molecular weight mineral oil additives, those with dispersing properties being regarded as of special interest. They may also be used as plastifiers for certain plastic materials. Their advantages include low migration and absence of  
10 toxicity. The use of polar/non-polar monomers advantageously results in greater applicational possibilities.

The following Examples serve to explain the invention.  
15 In so doing, the physical data are determined using the following standard specifications:

Viscosity :  $\eta$  (100°C) (according to DIN 51 562 or  
20 ASTM D 445 in the Ubbelohde-capillary viscosimeter)  
: VIB calculated from the 40 and 100° viscosity of the base oil  
Pour point: in the pour point automat according to DIN 51 583,  
25 Molar weight: (by gel chromatography using PMMA as standard)  
Nonuniformity: U  
Refractive Index: According to DIN 51 774  
30 Noack index: According to DIN 51 581

The abbreviations used have the following meanings:  
"AMA" alkyl methacrylates, "PAO" polyalphaolefins, "TMA-  
OD-Esters" esters of trimethylol propane with adipic  
35 acid.



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## EXAMPLES

## - Process -

## 5 Example 1

1 mol of 1-decene (140 g) is heated to 160°C in the reaction vessel. A mixture of 0.5 mol of isodecyl methacrylate (113 g) and 0.5 mol of C12-C15 alkyl  
10 methacrylate with a 60% iso-content (136 g) is then allowed to flow in over 4 hours. After the feed, the mixture is polymerised out in batches for another 12 hours. During the total reaction time of 16 hours, with the exception of the last hour, di-tert.-butylperoxide  
15 is added as an initiator every 30 minutes, (here 30 batches, total amount of 2.8 wt.% based on the monomers).

At the end of the reaction the monomer yield is about  
20 98%.

The product is a colourless, oily liquid which is completely miscible with mineral oils, poly-olefins or ester oils.

25

## Product data:

 $\eta$  (100°C) = 45.1 mm<sup>2</sup>/s. $\eta$  (40°C) = 489.0 mm<sup>2</sup>/s.

VIB = 146

30 Pour point = -43.2°C

 $\bar{M}_w$  = 4 000 $\bar{M}_n$  = 1 790

U = 1.23

loss by evaporation according to Noack 4 - 5 wt.%

35

## Example 2

As in Example 1 but the methacrylate mixture is fed in



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over 1.5 hours.

Product data:

$\eta$  (100°C) = 94.9 mm<sup>2</sup>/s.

5  $\eta$  (40°C) = 1 210.8 mm<sup>2</sup>/s.

VIB = 164

Pour point = -33.6°C

$\bar{M}_w$  = 8 330

$\bar{M}_n$  = 2 280

10 U = 2.65

Monomer yield = 95%

Example 3

15 As in Example 1, but reaction temperature 140°C,  
initiator used: tert.-butylperbenzoate

Product data:

$\eta$  (100°C) = 87.8 mm<sup>2</sup>/s

20  $\eta$  (40°C) = 1 188.3 mm<sup>2</sup>/s.

VIB = 154

Pour point = -34.7°C

$\bar{M}_w$  = 6 890

$\bar{M}_n$  = 2 240

25 U = 2.00

Monomer yield = 97%

Example 4

30 2 mol of 1-decene (280 g) is heated to 160°C in the  
reaction vessel. 1 mol of isodecyl methacrylate (227 g)  
is allowed to flow in at this temperature over 5 hours.  
At the end of the feed the mixture is further  
polymerised in batches for 6 hours. During the total  
35 reaction time, with the exception of the last hour, di-  
tert-butylperoxide is added as initiator every 30  
minutes (here: 20 portions, a total of 4.3 wt.% based on  
the monomers). When the reaction has finished, the



monomer yield is about 92%.

Product data:

5  $\eta$  (100°C) = 25.9 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 250.3 mm<sup>2</sup>/s.  
VIB = 134  
Pour point = -48.4°C  
 $\bar{M}_w$  = 2 240  
 $\bar{M}_n$  = 1 370  
10 U = 0.64

Example 5

As in Example 4 but using isodecyl methacrylate/decene  
15 1 : 1 mol, total initiator amount 2.8 wt.%.

Product data:

$\eta$  (100°C) = 47.6 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 603.8 mm<sup>2</sup>/s.  
20 VIB = 132  
Pour point = -38.9°C  
 $\bar{M}_w$  = 3120  
 $\bar{M}_n$  = 1 610  
U = 0.94

25

Example 6

As in Example 4, but using isodecyl methacrylate/decene  
in a mol ratio of 1 : 0.25, total initiator amount 2.8  
30 wt.%.

Product data:

$\eta$  (100°C) = 424.6 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 1 219.7 mm<sup>2</sup>/s.  
35 VIB = 170  
Pour point = -10.7°C  
 $\bar{M}_w$  = 12 300  
 $\bar{M}_n$  = 2 890



U = 3.26

Monomer yield = 98%

#### Example 7

5

As in Example 6, but introducing isodecyl methacrylates over 2.5 hours, total initiator amount: 2.8 wt.%.

Product data:

10  $\eta$  (100°C) = 888.2 mm<sup>2</sup>/s

$\eta$  (40°C) = 27162 mm<sup>2</sup>/s.

VIB = 206

Pour point: (too viscous)

$\bar{M}_w$  = 24 800

15  $\bar{M}_n$  = 3 480

U = 6.12

Monomer yield > 99%

#### Example 8

20

As in Example 5, but reaction temperature 140°C, initiator: tert.-butylperbenzoate 4.8 wt.%.

Product data:

25  $\eta$  = (100°C) = 130.7 mm<sup>2</sup>/s

$\eta$  = (40°C) = 2 335.1 mm<sup>2</sup>/s.

VIB = 147

Pour point: -25.9°C

$\bar{M}_w$  = 6 690

30  $\bar{M}_n$  = 2 200

U = 2.04

Monomer yield = 96%

#### Example 9

35

As in Example 5, but reaction temperature 126°C, initiator: tert.-butylpernonoate 4.8 wt.%.



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## Product data:

$$\eta (100^{\circ}\text{C}) = 460.1 \text{ mm}^2/\text{s}$$

$$\eta (40^{\circ}\text{C}) = 12321.7 \text{ mm}^2/\text{s}.$$

$$\text{VIB} = 180$$

5      Pour point =  $-8.5^{\circ}\text{C}$

$$\bar{M}_w = 11\,800$$

$$\bar{M}_n = 2\,560$$

$$U = 2.31$$

$$\text{Monomer yield} = 88\%$$

10

## Example 10

As in Example 4, but using in addition to 1 mol of  
1-decene in the preparation mixture, also 280 g of  
15      synthesis oil as solvent, prepared according to Example  
4.

## Product data:

$$\eta (100^{\circ}\text{C}) = 28.0 \text{ mm}^2/\text{s}$$

20       $\eta (40^{\circ}\text{C}) = 294.0 \text{ mm}^2/\text{s}.$

$$\text{VIB} = 127$$

$$\text{Pour point} = -44.5^{\circ}\text{C}$$

$$\bar{M}_w = 2\,180$$

$$\bar{M}_n = 1\,350$$

25       $U = 0.61$

$$\text{Monomer yield} = 98\%$$

## Example 11

30      As Example 1, but methacrylate component used is butyl  
methacrylate, feed time 3.5 hours

## Product data:

$$\eta (100^{\circ}\text{C}) = 1\,480 \text{ mm}^2/\text{s}$$

35       $\eta (40^{\circ}\text{C}) = 2\,836.2 \text{ mm}^2/\text{s}.$

$$\text{VIB} = 147$$

$$\text{Pour point: } -26^{\circ}\text{C}$$

$$\bar{M}_w = 6\,500$$



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 $\bar{M}_n = 1\ 860$  $U = 2.51$ 

Monomer yield = 91.%

## 5 Example 12

3 mol of dodecane (523 g) is heated to 160°C in the reaction vessel, 1 mol of C12-C15-alkyl methacrylate with a 90% iso-content (272 g) is allowed to rotate for 10 5.5 hours. At the end of the feed, the mixture is repolymerised in the batch for 11 hours. The initiator is added as described in Example 1. After the reaction the solvent is removed by distillation. The product 15 obtained is a colourless, oily liquid which is completely miscible with mineral oils, PAO or ester oils.

Product data:

 $\eta$  (100°C) = 16.7 mm<sup>2</sup>/s20  $\eta$  (40°C) = 128.1 mm<sup>2</sup>/s.

VIB = 141

Pour point: &lt; -52.1°C

 $\bar{M}_w = 1\ 510$  $\bar{M}_n = 1\ 230$ 25  $U = 0.23$ 

loss by evaporation according to Noack = 6%

Monomer yield = 95%

## 30 Example 13

As in Example 12, but instead of dodecane the same amount by weight of hydrocrack oil is used as solvent.

Product data hydrocrack oil:

35  $\eta$  (100°C) = 3.62 mm<sup>2</sup>/s

VIB = 126

Pour point = -33.0°C



Product data of the oligomer/oil mixture obtained:

$\eta$  (100°C) = 5.08 mm<sup>2</sup>/s

$\eta$  (40°C) = 24.1 mm<sup>2</sup>/s

VIB = 144

5 Pour point = -34.5°C

#### Example 14

10 400 g (0.28 mol) Cl\* is dissolved in 450 g (1.99 mol) of  
isodecyl methacrylate. 250 g (1.78 mol) of 1-decene is  
heated to 140°C in the reaction vessel. During 1.5  
hours the methacrylate mixture is allowed to flow in.  
At the end of the feed, the mixture is repolymerised in  
the batch for 15 hours. The initiator is added as  
15 described in Example 1. The initiator is tert-  
butylperbenzoate, total amount ~ 3 wt.%. The product  
obtained is a yellowish oil which is soluble in mineral  
oil.

20 \* Cl is the methacrylic acid ester of an ethoxylated  
C16-C18 fatty alcohol mixture, average degree of  
ethoxylation of 25. The alcohol used here is Marlipal  
1618/25®, the product made by Hüls AG.

25

Product data:

$\eta$  (100°C) = 1 006 mm<sup>2</sup>/s

$\eta$  (40°C) = 15 756 mm<sup>2</sup>/s.

VIB = 276

30 Pour point: (too viscous)

$\bar{M}_w$ ,  $\bar{M}_n$  = cannot be determined via GPC because of high  
absorption.

Yield: > 98%

#### 35 Example 15

300 g (0.37 mol) of component C2\*\* is dissolved in 400 g  
(1.77 mol) of isodecyl methacrylate. 300 g (214 mol) of



1-decene is heated to 160°C in the reaction vessel. The methacrylate mixture is allowed to flow in over 2 hours. Total reaction time 16.5 hours, addition of initiator as in Example 1. Initiator: di-tert.-butylperoxide, total amount ~ 3 wt.%. The product is soluble in mineral oil.

\*\* C2 is the methacrylic acid ester of methoxy polyethylene glycol with an average degree of ethoxylation of 16. The alcohol used here is Carbowax 750® (trademark of Union Carbide).

Product data:

$\eta$  (100°C) = 293.4 mm<sup>2</sup>/s

$\eta$  (40°C) = 3 999.0 mm<sup>2</sup>/s.

VIB = 217

Pour point = -22.1°C

$\bar{M}_w$ ,  $\bar{M}_n$  cannot be determined via GPC because of high absorption.

Yield about 100%

Example 16

As in Example 5, but instead of isodecyl methacrylate, C12-C15-alkyl methacrylate with 90% iso-content is used.

Product data:

$\eta$  (100°C) = 41.8 mm<sup>2</sup>/s

$\eta$  (40°C) = 417.6 mm<sup>2</sup>/s.

VIB 152

Pour point = -44.1°C

$\bar{M}_w$  = 3 430

$\bar{M}_n$  = 1 830

U = 0.78

Example 17

As in Example 1, but methacrylate component is C12-C15 alkyl methacrylate (90% iso), AMA/decene-ratio: 1 : 0.5



mol, AMA fed in for 1 hour.

Product data:

$\eta$  (100°C) = 234.4 mm<sup>2</sup>/s

5  $\eta$  (40°C) = 4 810.6 mm<sup>2</sup>/s.

VIB = 165

Pour point = -25.6°C

$\bar{M}_w$  = 23 100

$\bar{M}_n$  = 3 230

10 U = 6.14

Practical Examples

Example 18

15

Comparing the viscosity data of an oligomer/ester oil mixture with those of a poly- $\alpha$ -olefin/ester oil mixture.

|                   | 20% PAO 100 in<br>TMA-OD®-ester | 20% oligomer from<br>Example 17 in<br>TMA-OD®-ester |
|-------------------|---------------------------------|-----------------------------------------------------|
| 20 $\eta$ (100°C) | 6.68 mm <sup>2</sup> /s         | 7.70 mm <sup>2</sup> /s                             |
| VIB               | 193                             | 212                                                 |
| CCS (-30°C)       | 1 800 mPa s                     | 1 600 mPa s                                         |

25 It is clearly apparent that with cooligomers in the mixture a lower viscosity may be achieved at -30°C, despite the higher viscosity at 100°, thereby obtaining a better low-temperature behaviour.

Example 19

30

Comparing an oligomer/PAO formulation with a PAO6/PAO40 formulation when carrying out an MOT for a VW.



|    | PAO40 in PAO 6 | Oligomer from<br>Example 18 in<br>PAO6 |                                    |
|----|----------------|----------------------------------------|------------------------------------|
| 5  |                |                                        |                                    |
|    | Formulation    | 45% PAO 40                             | 45% oligomer                       |
|    |                | 14.2% commercially<br>available DI     | 14.2% commercially<br>available DI |
| 10 |                | package                                | package                            |
|    |                | 40.8% PAO6                             | 40.8 PAO6                          |
|    | $\eta$ (100°C) | 19.5 mm <sup>2</sup> /s                | 18.7 mm <sup>2</sup> /s            |
|    | VI             | 147                                    | 148                                |
|    | SAE-class      | 10W-50                                 | 10W-50                             |
| 15 | VW-MOT result  | 63.7 points,                           | 67.2 points, all                   |
|    | rings free     | all rings free                         |                                    |

20 Excellent diesel specifications can therefore be obtained with the oligomer/PAO mixture which results in good thermo-oxidative stability. It must also be noted that the pure polyalphaolefin formulation used for the purpose of comparison has an excellent diesel performance, as known.

Claims

1. A process for preparing oligomers and cooligomers by means of radical polymerisation of at least one monomer component B) with a higher polymerisation tendency and 0 - 90 wt.% based on the oligomers of a monomer component A) with a lower polymerisation tendency, at an elevated temperature and in the presence of polymerisation initiators using a conventional polymerisation vessel, characterised in that
- a) a liquid phase comprising the monomer component A) or a solvent L or both is introduced to a polymerisation vessel, and is heated to the reaction temperature.
- b) the component B) with the higher polymerisation tendency is added, provided the component A) has been introduced, so that the molar ratio of the component B) to component A), passes through values of 0 to about 0.2 in the initial phase of polymerisation and reaches the value 0.2 to 20 in the final phase of polymerisation with the proviso that
- c) the reaction temperature is chosen within a range in which there is already a significant depolymerisation of a homopolymer comprising the more easily polymerisable monomer component B) and
- d) an initiator I is added throughout the entire polymerisation, initiator I being chosen such that the half-life periods at the relevant reaction temperature are 1 minute to about 5 hours, and the initiator amounts are 0.1 to 10 wt.% based on the total amount of monomers.

2. A process according to claim 1, characterised in





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that A) the Q-values (according to Alfrey-Price) of the monomers A) with the lower polymerisation tendency differ from those of the monomers B) with the higher polymerisation tendency by a factor  $\geq 5$ .

5

3. A process according to claims 1 and 2, characterised in that the range in which there is already a significant depolymerisation of a homopolymer comprising component B) is a range in which 3 - 80 wt.% of monomers (based on the sum of monomers + polymer) are registered under monomer/polymer equilibrium conditions.

10

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## Abstract

- The invention relates to a process for preparing oligomers and cooligomers by means of radical polymerisation of at least one monomer component B) with a higher polymerisation tendency and 0 - 90 wt.% (based on the oligomers) of a monomer component A) with a lower polymerisation tendency at an elevated temperature and in the presence of polymerisation initiators, in a conventional polymerisation vessel, in which
- a) a liquid phase comprising a monomer component A) or a solvent L or both is introduced to the polymerisation vessel, and the phase is heated to the reaction temperature,
  - b) the component B) with the higher polymerisation tendency is added after component A) has been introduced, so that the molar ratio between B) and component A) passes through values of 0 to about 0.2 in the initial phase of polymerisation and has the value of 0.2 to 20 in the end phase of polymerisation, with the proviso that
  - c) the reaction temperature is chosen within a region in which there is already a significant depolymerisation of a homopolymer comprising the monomer component B) which polymerises more easily and
  - d) an initiator I is added throughout the entire polymerisation, the initiator I being such that the half-life periods are 1 minute to about 5 hours at the relevant reaction temperature and the initiator amounts are 0.1 to 10 wt.% based on the total amount of monomers.



## PROCESS FOR PREPARING HOMOLIGOMERS AND COOLIGOMERS

## Description

## 5 Area of the invention

The invention relates to a process for preparing homo- and cooligomers, especially cooligomers of (meth)acrylic acid esters and  $\alpha$ -olefins which may be used as synthesis  
10 oils or components of such oils, as mineral oil additives as well as plastifiers and the like.

## Prior art

15 In general, oligomers are compounds with a molecular weight of from  $10^2$  -  $10^5$ , especially  $10^2$  -  $10^4$ , which are synthesised from corresponding monomer units. (cf. Römpp's Chemie-Lexikon, 8th Ed., p. 2893, Franckh'sche  
20 Verlagsbuchh. 1985). Prior art examples, on which this invention is based, include cooligomers of (meth)acrylic acid esters and  $\alpha$ -olefins. Oligomers of acrylic acid esters, as understood nowadays, are disclosed, for example, in C.E. Rehberg et al. in Ind. Eng. Chem. 44  
(12) 2864, 1952).

25

US-A 3 968 148 or DE-A 22 43 064 describe, for example, this type of oligomer which are synthesised from three monomer groups. These oligomers comprise:  
about 10 - 90 wt.% of an 1-alkene having 4 to 32 C-atoms  
30 about 1 - 35 wt.% of one or more alkyl(meth)acrylic acid esters having 8 to 34 C-atoms in the alkyl group and  
about 1 - 35 wt.% of one or more alkyl esters of  
(meth)acrylic acid or homologous,  
35 terminally unsaturated carboxylic acids having 1 to 4 C-atoms in the alkyl group.

Oligomers of this kind preferably have a molecular weight of  $M_n = 1,000$  to  $4,000$ . Mention must be made of the narrow molecular weight range and of the high uniformity of the products. US-A 4 009 195 also

5 discloses an oligomerisation process, in which various (meth)acrylic acid derivatives such as C1-C4-alkyl esters in amounts of 1 to 35 wt.% and (meth)acrylic acid esters of C8-C34-alkanols in amounts of 1 to 45 wt.%, are continuously and simultaneously added to a mixture

10 of radical initiators and 10 to 90 wt.% of a 1-alkene having 4 to 32 C-atoms, so that the molar ratio, which arises more or less immediately, between acid derivatives and 1-alkene is kept relatively constant in the reaction preparation within a range of 0.001 to 0.2.

15 The addition, here, should be at a temperature which does not affect oligomerisation. The yields are given as 40 to 70%, the residue, in particular, being  $\alpha$ -olefin.

20 Furthermore, DE-A 32 23 694 discloses copolymers of  $\alpha$ - $\beta$ -unsaturated dicarboxylic acid esters with  $\alpha$ -olefins. By definition, the  $\alpha$ - $\beta$ -unsaturated dicarboxylic acid esters contain, as alcohol component, straight-chained or branched monoalcohols having 3 to 10 carbon atoms;

25 the  $\alpha$ -olefins have 10 to 16 carbon atoms. The copolymers, may, optionally, be crosslinked and their pour-point must be between  $-60$  and  $0^\circ\text{C}$ .

US-A 4 526 950 discloses a method for preparing

30 copolymers, in which the mixture of the components, based on at least one  $\alpha$ -olefin having at least 6 C-atoms, and at least one unsaturated carboxylic acid or derivatives copolymerisable with olefins, is heated to at least  $135^\circ\text{C}$  in the presence of a radical initiator

35 and in the absence of solvents or diluents. Here, none of the reactive monomers is used in excess in order to avoid a dilution of activity. SU-A 1 135 752 also discloses copolymers comprising decyl methacrylate and

tetradecene with a molar weight of 8,000 to 13,000, which are used as thickening agents in lubricating oil.

5 EP-A 217 602 describes oil additives based on ethylene copolymers which comprise inter alia ethylenically unsaturated mono- or dicarboxylic acids and the esters thereof which have a molar weight of  $M_n < 1,000$ .

#### Object and solution

10

One method for reducing the molecular weight in the radical polymerisation of monomers is the use of regulators, especially mercaptans (cf. G. Henrici-Olivé et al. Fortschr. Hochpolym. Forsch. Vol. 2., p. 496 - 15 577 (1961); Houben-Weyl, Methoden der Organ. Chemie, 4th ed., vol. XIV/I).

A further suitable method described in the literature is the overdosing of catalyst. This, however, makes the 20 process more expensive. Furthermore, experiments have been carried out for obtaining oligomers of methyl methacrylate during heating in the liquid phase above 160°C, in the presence of an inhibitor. Experience shows that an increase in temperature and in pressure 25 and longer reaction times promote the formation of higher oligomers. (Houben-Weyl, 4th ed., vol. XIV/I p. 1046, 1072 - 1073, Georg-Thieme-Verlag 1961).

30 However, process conditions which are too drastic should not be used for a technical process which is, moreover, based on the exothermic radical polymerisation. Yet, if the prior art preparation of oligomers or cooligomers comprising (meth)acrylic acid esters and  $\alpha$ -olefins, is used, for example, the lack of generally applicable 35 process rules which ensure constant success is apparent. The processes shown were also not able to fully satisfy the requirements in individual cases. The prior art application of (meth)acrylate oligomers is characterised

by:

- 5       - the apparatus used, in particular for the anionic polymerisation, is necessarily expensive, since the operation takes place under inert conditions; relatively pure monomers are needed; use of a solvent is standard procedure.
- 10       - when regulators are used in radical reactions, commonly known problems occur with the incorporation of terminal groups as, for example, in the case of mercaptans.
- 15       - furthermore, high concentrations of initiator are used. Apart from the considerable costs involve, it also means a greater safety risk.

20       It has now been found that the process of this invention makes cooligomers, especially those of (meth)acrylic acid and  $\alpha$ -olefins significantly more accessible.

25       This invention relates to a process which makes it possible to homopolymerise (meth)acrylates or copolymerise them with further monomers and in which the molecular weights may be adjusted over a wide range which covers the entire oligomer range and even extends beyond it. No regulator is used here. The amount of initiator used is normally not greater than the amount usually needed for solution polymerisations. The

30       molecular weight adjustment to obtain lower molecular weights, in particular, is not predominantly effected by varying the amount of initiator used, as is disclosed in the prior art.

35       The systems described comprise a component B), which has a higher polymerisation tendency (such as (meth)acrylates), plus a component A), which has a lower polymerisation tendency, and/or a suitable solvent L.

The molecular weight of the oligomers, right down to the lower molecular oligomers including dimers/trimers, is regulated via the following variables:

- 5     α)   The ratio of B) to A) or to A) plus L or to L alone. Under otherwise similar conditions, with a larger amount of A) and/or L or A) alone, lower molecular weights are obtained.
- 10    β)   The feed time for B). If the feed times are increased, lower molecular weights are obtained under the same conditions.
- 15     γ)   The reaction temperature which is selected within a range in which a conventionally prepared, regulator-free homopolymer of the more polymerisable component B) depolymerises to a noticeable degree. This means that at the chosen temperature, in the monomer/polymer equilibrium, there are already larger amounts of monomer, normally 3 to 80 wt.%, especially 10 to 60 wt.%. Thus, depending on the required molecular weight range for n-decyl methacrylate, for example, a suitable temperature range is from 120°C to 170°C, in which between 3 and 80 wt.% of the monomers are in equilibrium. A temperature, at which there are between 15% and 50% of monomers (here 140 to 160°C) is particularly suitable for molecular weights  $\bar{M}_w$  in the lower molecular weight range with simultaneously high yield. In this way, depending on the chosen reaction temperature, the formation of long B) sequences may be suppressed to a greater or lesser extent which means that in addition to α) and β) the molecular weight may be effectively controlled by lowering the reaction temperature in the above range, the molecular weights of the (co)oligomers thereby being increased.
- 20
- 25
- 30
- 35

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By varying  $\alpha$ ),  $\beta$ ) and  $\gamma$ ) it is possible to adjust the molecular weights of about 500 to 100,000 in a simple and reproducible manner without using regulators.

Through a correct choice of the parameters, including  
5 the total reaction time, a complete reaction of the monomers may also be achieved easily. Thus, the process according to the invention has the further advantage that the residual monomers do not have to be separated (see Examples). If the formulation is such that apart  
10 from A) no further "solvent" is used and A) is completely reacted which is easily possible (see Examples), a further working up of the preparation mixture may be dispensed with. If in formulations with an inert solvent, a solvent L is chosen which may remain  
15 in the product such as PAO or mineral oil for which oligomers are used as the synthetic component of the base oil, or previously prepared oligomer is used as solvent for preparing further oligomer, the separation of the solvent may also be dispensed with (Examples 10  
20 and 13).

Thus, this invention relates to a process for preparing oligomers and cooligomers through radical polymerisation with at least one monomer component B) with a higher  
25 polymerisation tendency and 0 to 90 wt.%, preferably 1 to 50 wt.% (based on the oligomers) of a monomer component A) with a lower polymerisation tendency, at an elevated temperature and in the presence of polymerisation initiators in a conventional  
30 polymerisation vessel, whereby:

- a) a liquid phase comprising the monomer component A) or a solvent L or both is introduced into the polymerisation vessel and heated to the reaction  
35 temperature.
- b) the component B) with a higher polymerisation tendency is added after the component A) has been

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introduced, so that the molar ratio between the components B) and A) passes through values of from 0 to about 0.2 in the initial phase of the polymerisation and achieves the value of 0.2 to 20 in the end phase of the polymerisation, with the proviso that

- 5
- 10
- 15
- 20
- 25
- c) the reaction temperature is chosen within a range in which there is already a significant depolymerisation of the homopolymer (prepared without regulator) comprising the monomer component B) which has better polymerisation characteristics. In order to determine a "significant depolymerisation" please note that under these temperature conditions there are already larger amounts of monomers, normally 3 to 80 wt.%, in particular 10 to 60 wt.%, especially 15 to 50 wt.% (based on the sum of the monomers plus polymer) in the monomer/polymer equilibrium,
- d) the initiator I is added throughout the entire polymerisation, the initiator I being selected such that the half life at the corresponding reaction temperature is one minute to about five hours and the amount of initiator used is 0.1 to 10, preferably 1 to 5 wt.% based on the total amount of monomers.

30 Normally, the skilled man has sufficient know-how from the prior art literature (e.g. K Wachstum)

K Abbruch

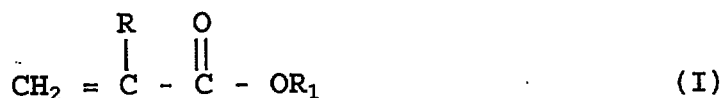
35 in order to differentiate between monomers with a high radical polymerisation tendency B) or C) and those with a lower polymerisation tendency (Monomer A). One way of assessing the relevant polymerisation tendency is, for example, the use of the widely differing Q-values of the monomers (according to Alfrey-Price, cf. Brandrup-Immergut Polymer Handbook loc.cit. II/267). Generally,

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it may be assumed that the monomers have either a higher or lower polymerisation tendency, if the two numerical values of Q differ from each other by a factor  $\geq 5$ . 1-Hexene as monomer component A) has, for example, a Q-value of 0.035, butyl methacrylate, for example, has the Q-value of 0.82.

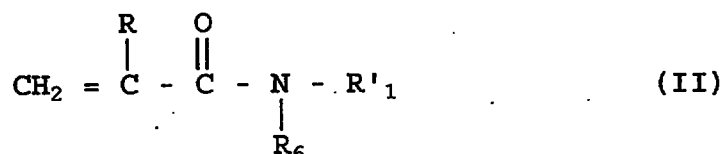
According to the invention, the monomer component A), to be used in amounts of 0 to 90 wt.%, preferably comprises at least one radically polymerisable  $\alpha$ -olefin having 4 to 40 carbon atoms, here, the cooligomer composition of CM normally comprises 5 to 90 wt.% of A), the remainder being B) (= cooligomers CM'). Preferably, the component B) comprises at least one acrylic or methacrylic acid ester of Formula (I)



wherein R is hydrogen or methyl and  $\text{R}_1$  may be an optionally branched, optionally cyclic alkyl group having 1 to 42 carbon atoms, in which individual chain members may be substituted by ether groups -O-, in which there is a spacing of at least two carbon chain members between the individual ether groups, in which  $\text{R}_1$  may additionally be substituted by one or more functional groups Y which comprise at least one nitrogen or oxygen atom bound to carbon. Preferably, Y is a  $-\text{NR}_2\text{R}_3$ ,  $-\text{OR}_4$ ,  $-\text{COOR}_5$  or  $-\text{C}-\text{CH}-$  group, wherein  $\text{R}_2$  and

$\text{R}_3$ , independently of each other, are alkyl groups with 1 to 4 carbon atoms, wherein  $\text{R}_2$  and  $\text{R}_3$ , together with the nitrogen and optionally further nitrogen or oxygen atoms may be a 5- or 6-membered ring, and wherein  $\text{R}_4$  and  $\text{R}_5$  are hydrogen or an alkyl or cycloalkyl group with 1 to 40, preferably 1 to 10, carbon atoms. If cycloalkyl groups are present, they are preferably 5- to 8-membered ring

systems. Furthermore, the component B) may comprise monomers of Formula II

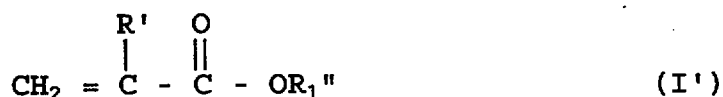


wherein R' and R'<sub>1</sub> have the meanings of R or R<sub>1</sub> and R<sub>6</sub> is hydrogen or has the same meaning as R<sub>1</sub>.

According to the invention, the process is particularly preferred for preparing homo-oligomers from the monomer component B), particularly (meth)acrylic acid esters of Formula (I) (see above), especially from the monomers B') (see below), more particularly from B'-α. Furthermore, the process according to the invention is preferably used for preparing cooligomers CM", synthesised from

A) 0 to 75 wt.%, preferably 10 to 40 wt.% of at least an 1-alkene having 4 to 32 carbon atoms, preferably 10 to 14 carbon atoms in the molecule and

B'-α) 20 to 100 wt.%, preferably 40 to 90 wt.% of at least one (meth)acrylic acid ester of Formula I'



wherein R' is hydrogen or methyl and R<sub>1</sub>" is an optionally branched alkyl group or a cycloalkyl group having 4 to 32 carbon atoms, preferably 8 to 20 carbon atoms in the alkyl group and

B'-β) 0 to 65 wt.%, preferably 0.5 to 50, more particularly 3 to 40 wt.%, of a (meth)acrylic acid ester of Formula I"

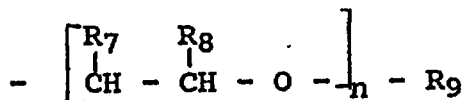
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5 wherein R' is hydrogen or methyl and R<sub>1</sub>'' is an alkyl group with 2 to 6 carbon atoms, substituted with at least one group Y', wherein Y' has the same meaning as Y, more particularly substituted with a hydroxyl group, or R<sub>1</sub>'' is a group

10



15

wherein R<sub>7</sub> and R<sub>8</sub> are hydrogen or methyl, R<sub>9</sub> is hydrogen or an optionally branched alkyl group with 1 to 40, preferably 1 to 20 carbon atoms, and n is an integer from 1 to 60, with the proviso that if n is 1, R<sub>8</sub> is at the same time only an optionally branched alkyl group having 1 to 40 carbon atoms.

20

The components A') and B') of the cooligomers normally make up 100 wt.%. Examples of the monomer component A) include:

25

butene-1, pentene-1, hexane-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadene-1, octadecene-1, nonadecene-1, eicosene-1, heneicosene-1, docosene-1-, trocosene-1, tetracosene-1, pentacosene-1, 30 hexacosene-1, heptacosene-1, octacosene-1, nonacosene-1, triacontene-1, hentriacontene-1, dotriacontene-1, or the like. Suitable monomer components also include branched alkenes such as vinylcyclohexane, 3,3-dimethylbutene-1, 35 3-methylbutene-1, diisobutylene-4-methylpentene-1 or the like. 1-Alkenes with 10 to 32 carbon atoms, which are obtained during the polymerisation of ethylene, propylene or mixtures thereof, are also suitable. These materials, themselves, are obtained from hydrocracked

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substances.

The variant in which component A) of the cooligomers CM is 1-decene or dodecene, tetradecene is particularly preferred. Also of special interest are oligomers or cooligomers CM wherein component B) comprises (meth)acrylic acid esters having 4 to 22 carbon atoms in the (branched or unbranched) alkyl group, or mixtures thereof.

Examples of monomers include e.g.:

butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, isodecyl acrylate, decyl acrylate, undecyl acrylate, dodecyl acrylate, tridecyl acrylate, tetradecyl acrylate, pentadecyl acrylate, hexadecyl acrylate, heptadecyl acrylate, octadecyl acrylate, cetylstearyl acrylate, oleyl acrylate, nonadecyl acrylate, eicosyl acrylate, cetyleicosyl acrylate, stearyleicosyl acrylate, docosyl acrylate, eicosyltetraatriacontyl acrylate or the corresponding methacrylates. Special mention must be made alkyl methacrylates with  $> C_{10}$  in the alkyl group which have a higher iso content. These include, for example,  $C_{12}$ - $C_{15}$ -alkylesters of methacrylic acid with an iso content of about 60 to 90%, as well as isodecyl methacrylate. For certain applications it is also possible to use monomers according to Formula I, wherein  $R_1$  is  $C_1$ - $C_3$ -alkyl, in particular methyl methacrylate in addition to ethyl acrylate, ethyl methacrylate, propyl acrylate and propyl methacrylate. Here, however, the lower boiling points have a limiting effect on the reaction at normal pressure.

Examples of the monomer group B) of Formula I also include the following amino-substituted alkyl esters of (meth)acrylic acid:

- 2-diaminomethyl (meth)acrylate,  
2-diethylaminoethyl (meth)acrylate,  
3-dimethylamino-2,2-dimethylpropyl-1- (meth)acrylate,  
3-dimethylamino-2,2-dimethylpropyl-1- (meth)acrylate,  
5 2-morpholinoethyl (meth)acrylate,  
2-tert.-butylaminoethyl (meth)acrylate,  
3-(dimethylamino)propyl (meth)acrylate,  
2-(dimethylaminoethoxy-ethyl) (meth)acrylate.
- 10 Mention must also be made of the following oxy- or  
alkoxy-substituted alkyl esters of (meth)acrylic acid :  
2-hydroxyethyl (meth)acrylate,  
2-hydroxypropyl (meth)acrylate,  
2-methoxyethyl (meth)acrylate,  
15 2-ethoxyethyl (meth)acrylate,  
2-butoxyethyl (meth)acrylate,  
2-(2-butoxyethoxy)ethyl methacrylate,  
2-(ethoxyethyloxy)ethyl (meth)acrylate,  
4-hydroxybutyl (meth)acrylate,  
20 2-[2-(2-ethoxyethoxy)ethoxy]ethyl (meth)acrylate,  
3-methoxybutyl-1- (meth)acrylate,  
2-alkoxy-methylethyl (meth)acrylate,  
2-hexoxyethyl (meth)acrylate.
- 25 Examples of the monomer group B) of Formula (II) include  
the following (meth)acrylamides:  
N-methyl (meth)acrylamide,  
N-dimethylamino (meth)acrylamide,  
N-dimethylaminopropyl (meth)acrylamide,  
30 N-isopropyl (meth)acrylamide,  
N-tert.butyl (meth)acrylamide,  
N-isobutylmethyl (meth)acrylamide,  
N-decyl (meth)acrylamide, N-cyclohexyl (meth)acrylamide,  
N-[3-(dimethylamino)-2,2-dimethylpropyl]-methacrylamide,  
35 N-dodecyl (meth)acrylamide,  
N-[3-dimethylaminopropyl] (meth)acrylamide,  
N-[2-hydroxyethyl] (meth)acrylamide.

The solvent L used for the monomers must be stable and inert under the chosen reaction conditions. Generally, in order to avoid any pressure reactions, the boiling point must be above the chosen reaction temperature.

5 Solvents of this kind are known per se.

#### Preparing cooligomers CM

10 As already stated, the preparation of oligomers or cooligomers from the two monomer classes is known per se, using radical-induced polymerisation e.g. thermal polymerisation and whilst adding a suitable initiator and/or Redox system (cf. prior art). The process of the invention may be used for preparing cooligomers CM which  
15 are either new or whose comonomer composition is known. The process according to the invention is noted for its great applicational possibilities and excellent results, but certain process conditions must be maintained. During the process, the monomer component A) with a low  
20 polymerisation tendency and/or the solvent L are heated to a reaction temperature in a suitable polymerisation vessel equipped with thermometer, heating and stirring devices. The solvent L must be stable and inert under the reaction conditions. The boiling point is  
25 preferably above the chosen reaction temperature. Examples of solvents include aliphatic or aromatic hydrocarbons, such as xylene or cymene, decane or dodecane, but mineral oils, polyalphaolefins, esters and previously prepared oligomers are also suitable as  
30 solvents.

The use of mineral oils or other non-mineral oil based synthesis oil liquids, is of particular advantage if the cooligomers are intended to be used as base liquids for  
35 synthesis oils (cf. Ullmann's Encyclopädie der Techn. Chemie, 4th Ed., Vol. 20, p. 454 - 530, Verlag Chemie 1981), in particular the types later to be used as mixing components. Here, mention must be made of

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polyalphaolefins of various viscosity classes, hydrocrack oils, various ester oils such as TMA-OD-esters as well as commercially available mineral oils such as of the 100N or 150N-class.

5

According to feature C), the reaction temperature is chosen within a range in which a homopolymer (prepared without regulator) from a monomer component B) which has better polymerisation characteristics depolymerises to a  
10 noticeable extent. A "noticeable depolymerisation" normally exists when there are already large amounts of monomers in the (thermally related) monomer/polymer equilibrium. As a guide, there is 3 to 80 wt.% of monomer in the equilibrium. However, there are certain  
15 requirements for determining the polymerisation/depolymerisation equilibria and no data exist as yet in respect of a number of monomers or temperature regions. In order to give a rough but practical estimate of the temperature range suitable for  
20 the process, the simple method of thermogravimetry has proved useful. Here, a conventionally prepared homopolymer of the more easily polymerisable component B) is examined at increasing temperature, under oxygen exclusion using thermogravimetry. In order to carry  
25 out preliminary oligomerisation experiments, the temperature range should be considered which starts at 50°C below the temperature at which the first weight losses occur because of depolymerisation, and which ends at about 30°C above this temperature.

30

According to the invention, the selection and mode of feed of the radical initiators I are also important: the initiators I selected must have a half-life at the corresponding reaction temperature of from about 1  
35 minute to about 5 hours. (Cf. Kirk-Othmer, 3rd. Ed. Vol. 13. pg. 355 - 373, Interscience 1981; Brandrup-Immergut, Polymer Handbook loc.cit. II/1).

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The initiators are introduced during the entire polymerisation (with the exception of the final polymerisation which mostly takes 30 minutes to 1 hour).

The reaction normally takes about 10 to 15 hours, for example about  $12 \pm 1$  hours. 1/10th up to half of this time, that is, 1 - 5.5 hours is normally taken up by the phase in which the monomer is fed in. The initiators are fed in during the entire reaction, preferably, either in batches at suitable intervals e.g. every half hour, or continuously e.g. by feed mode. The addition of 0.001 - 0.005 mol of initiator each per portion every half hour may be given as a guide (based on each mol of monomers A) or B)). The amount of initiator used is 0.1 to about 10 wt.% based on the total amount of monomers.

Suitable initiators are, for example, peroxide initiators, provided they meet the above criteria. They include di-tert.-butylperoxide tert.butylperbenzoate or tert. butylperoctoate, but these are only a few examples.

Based on present findings, according to the invention, a reaction of the monomers of e.g. 98% may be largely achieved by a suitable choice of the reaction conditions, so that in many cases the monomers need not be separated off or indeed further processed. In the remaining cases, the residual monomer comprises almost exclusively component A) which is separated off, depending on the application. The products are inter alia colourless oily liquids which are completely miscible with mineral oil, PAO, HC-oils and ester oils if the content of B'-  $\beta$  does not exceed certain limits e.g. 50 wt.%.

#### Advantageous characteristics

As already stated in the prior art, the cooligomers CM according to the invention may be used for various technical applications. They are suitable as valuable

components of synthesis oils. If they comprise functional groups (e.g. according to feature B'-  $\beta$ ), the synthesis oils exhibit dispersing activity.

5 Furthermore, they are used as low-molecular weight mineral oil additives, those with dispersing properties being regarded as of special interest. They may also be used as plastifiers for certain plastic materials. Their advantages include low migration and absence of  
10 toxicity. The use of polar/non-polar monomers advantageously results in greater applicational possibilities.

The following Examples serve to explain the invention.  
15 In so doing, the physical data are determined using the following standard specifications:

Viscosity :  $\eta$  (100°C) (according to DIN 51 562 or  
20 ASTM D 445 in the Ubbelohde-capillary viscosimeter).  
: VIB calculated from the 40 and 100° viscosity of the base oil  
Pour point: in the pour point automat according to DIN 51 583,  
25 Molar weight: (by gel chromatography using PMMA as standard)  
Nonuniformity: U  
Refractive Index: According to DIN 51 774  
30 Noack index: According to DIN 51 581

The abbreviations used have the following meanings:  
"AMA" alkyl methacrylates, "PAO" polyalphaolefins, "TMA-  
OD-Esters" esters of trimethylol propane with adipic  
35 acid.



## EXAMPLES

### - Process -

#### 5 Example 1

1 mol of 1-decene (140 g) is heated to 160°C in the reaction vessel. A mixture of 0.5 mol of isodecyl methacrylate (113 g) and 0.5 mol of C12-C15 alkyl  
10 methacrylate with a 60% iso-content (136 g) is then allowed to flow in over 4 hours. After the feed, the mixture is polymerised out in batches for another 12 hours. During the total reaction time of 16 hours, with the exception of the last hour, di-tert.-butylperoxide  
15 is added as an initiator every 30 minutes, (here 30 batches, total amount of 2.8 wt.% based on the monomers).

At the end of the reaction the monomer yield is about  
20 98%.

The product is a colourless, oily liquid which is completely miscible with mineral oils, poly-olefins or ester oils.

25

#### Product data:

$\eta$  (100°C) = 45.1 mm<sup>2</sup>/s.

$\eta$  (40°C) = 489.0 mm<sup>2</sup>/s.

VIB = 146

30 Pour point = -43.2°C

$\bar{M}_w$  = 4 000

$\bar{M}_n$  = 1 790

U = 1.23

loss by evaporation according to Noack 4 - 5 wt.%

35

#### Example 2

As in Example 1 but the methacrylate mixture is fed in

over 1.5 hours.

Product data:

- $\eta$  (100°C) = 94.9 mm<sup>2</sup>/s.  
 5  $\eta$  (40°C) = 1 210.8 mm<sup>2</sup>/s.  
 VIB = 164  
 Pour point = -33.6°C  
 $\bar{M}_w$  = 8 330  
 $\bar{M}_n$  = 2 280  
 10 U = 2.65  
 Monomer yield = 95%

Example 3

- 15 As in Example 1, but reaction temperature 140°C,  
 initiator used: tert.-butylperbenzoate

Product data:

- $\eta$  (100°C) = 87.8 mm<sup>2</sup>/s  
 20  $\eta$  (40°C) = 1 188.3 mm<sup>2</sup>/s.  
 VIB = 154  
 Pour point = -34.7°C  
 $\bar{M}_w$  = 6 890  
 $\bar{M}_n$  = 2 240  
 25 U = 2.00  
 Monomer yield = 97%

Example 4

- 30 2 mol of 1-decene (280 g) is heated to 160°C in the  
 reaction vessel. 1 mol of isodecyl methacrylate (227 g)  
 is allowed to flow in at this temperature over 5 hours.  
 At the end of the feed the mixture is further  
 polymerised in batches for 6 hours. During the total  
 35 reaction time, with the exception of the last hour, di-  
 tert-butylperoxide is added as initiator every 30  
 minutes (here: 20 portions, a total of 4.3 wt.% based on  
 the monomers). When the reaction has finished, the

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monomer yield is about 92%.

Product data:

$\eta$  (100°C) = 25.9 mm<sup>2</sup>/s  
5  $\eta$  (40°C) = 250.3 mm<sup>2</sup>/s.  
VIB = 134  
Pour point = -48.4°C  
 $\bar{M}_w$  = 2 240  
 $\bar{M}_n$  = 1 370  
10 U = 0.64

Example 5

As in Example 4 but using isodecyl methacrylate/decene  
15 1 : 1 mol, total initiator amount 2.8 wt.%.

Product data:

$\eta$  (100°C) = 47.6 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 603.8 mm<sup>2</sup>/s.  
20 VIB = 132  
Pour point = -38.9°C  
 $\bar{M}_w$  = 3120  
 $\bar{M}_n$  = 1 610  
U = 0.94

25

Example 6

As in Example 4, but using isodecyl methacrylate/decene  
in a mol ratio of 1 : 0.25, total initiator amount 2.8  
30 wt.%.

Product data:

$\eta$  (100°C) = 424.6 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 1 219.7 mm<sup>2</sup>/s.  
35 VIB = 170  
Pour point = -10.7°C  
 $\bar{M}_w$  = 12 300  
 $\bar{M}_n$  = 2 890

U = 3.26

Monomer yield = 98%

#### Example 7

5

As in Example 6, but introducing isodecyl methacrylates over 2.5 hours, total initiator amount: 2.8 wt.%.  
 10

Product data:

$\eta$  (100°C) = 888.2 mm<sup>2</sup>/s

$\eta$  (40°C) = 27162 mm<sup>2</sup>/s.

VIB = 206

Pour point: (too viscous)

$\bar{M}_w$  = 24 800

15  $\bar{M}_n$  = 3 480

U = 6.12

Monomer yield > 99%

#### Example 8

20

As in Example 5, but reaction temperature 140°C, initiator: tert.-butylperbenzoate 4.8 wt.%.  
 25

Product data:

$\eta$  = (100°C) = 130.7 mm<sup>2</sup>/s

$\eta$  = (40°C) = 2 335.1 mm<sup>2</sup>/s.

VIB = 147

Pour point: -25.9°C

$\bar{M}_w$  = 6 690

30  $\bar{M}_n$  = 2 200

U = 2.04

Monomer yield = 96%

#### Example 9

35

As in Example 5, but reaction temperature 126°C, initiator: tert.-butylpernonoate 4.8 wt.%.  
 40

## Product data:

 $\eta$  (100°C) = 460.1 mm<sup>2</sup>/s $\eta$  (40°C) = 12321.7 mm<sup>2</sup>/s.

VIB = 180

5 Pour point = -8.5°C

 $\bar{M}_w$  = 11 800 $\bar{M}_n$  = 2 560

U = 2.31

Monomer yield = 88%

10

## Example 10

As in Example 4, but using in addition to 1 mol of  
1-decene in the preparation mixture, also 280 g of

15 synthesis oil as solvent, prepared according to Example  
4.

## Product data:

 $\eta$  (100°C) = 28.0 mm<sup>2</sup>/s20  $\eta$  (40°C) = 294.0 mm<sup>2</sup>/s.

VIB = 127

Pour point = -44.5°C

 $\bar{M}_w$  = 2 180 $\bar{M}_n$  = 1 350

25 U = 0.61

Monomer yield = 98%

## Example 11

30 As Example 1, but methacrylate component used is butyl  
methacrylate, feed time 3.5 hours

## Product data:

 $\eta$  (100°C) = 1 480 mm<sup>2</sup>/s35  $\eta$  (40°C) = 2 836.2 mm<sup>2</sup>/s.

VIB = 147

Pour point: -26°C

 $\bar{M}_w$  = 6 500

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$\bar{M}_n = 1\ 860$

$U = 2.51$

Monomer yield = 91.%

# 5 Example 12

3 mol of dodecane (523 g) is heated to 160°C in the reaction vessel, 1 mol of C12-C15-alkyl methacrylate with a 90% iso-content (272 g) is allowed to rotate for 10 5.5 hours. At the end of the feed, the mixture is repolymerised in the batch for 11 hours. The initiator is added as described in Example 1. After the reaction the solvent is removed by distillation. The product 15 obtained is a colourless, oily liquid which is completely miscible with mineral oils, PAO or ester oils.

Product data:

20  $\eta$  (100°C) = 16.7 mm<sup>2</sup>/s  
 $\eta$  (40°C) = 128.1 mm<sup>2</sup>/s.  
VIB = 141

Pour point: < -52.1°C

$\bar{M}_w = 1\ 510$

$\bar{M}_n = 1\ 230$

25  $U = 0.23$

loss by evaporation according to Noack = 6%

Monomer yield = 95%

# 30 Example 13

As in Example 12, but instead of dodecane the same amount by weight of hydrocrack oil is used as solvent.

Product data hydrocrack oil:

35  $\eta$  (100°C) = 3.62 mm<sup>2</sup>/s

VIB = 126

Pour point = -33.0°C

Product data of the oligomer/oil mixture obtained:

$\eta$  (100°C) = 5.08 mm<sup>2</sup>/s

$\eta$  (40°C) = 24.1 mm<sup>2</sup>/s

VIB = 144

5 Pour point = -34.5°C

#### Example 14

10 400 g (0.28 mol) C1\* is dissolved in 450 g (1.99 mol) of isodecyl methacrylate. 250 g (1.78 mol) of 1-decene is heated to 140°C in the reaction vessel. During 1.5 hours the methacrylate mixture is allowed to flow in. At the end of the feed, the mixture is repolymerised in the batch for 15 hours. The initiator is added as described in Example 1. The initiator is tert-butylperbenzoate, total amount ~ 3 wt.%. The product obtained is a yellowish oil which is soluble in mineral oil.

20 \* C1 is the methacrylic acid ester of an ethoxylated C16-C18 fatty alcohol mixture, average degree of ethoxylation of 25. The alcohol used here is Marlupal 1618/25®, the product made by Hüls AG.

25

Product data:

$\eta$  (100°C) = 1 006 mm<sup>2</sup>/s

$\eta$  (40°C) = 15 756 mm<sup>2</sup>/s.

VIB = 276

30 Pour point: (too viscous)

$\bar{M}_w$ ,  $\bar{M}_n$  = cannot be determined via GPC because of high absorption.

Yield: > 98%

#### 35 Example 15

300 g (0.37 mol) of component C2\*\* is dissolved in 400 g (1.77 mol) of isodecyl methacrylate. 300 g (214 mol) of

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1-decene is heated to 160°C in the reaction vessel. The methacrylate mixture is allowed to flow in over 2 hours. Total reaction time 16.5 hours, addition of initiator as in Example 1. Initiator: di-tert.-butylperoxide, total amount ~ 3 wt.%. The product is soluble in mineral oil.

\*\* C2 is the methacrylic acid ester of methoxy polyethylene glycol with an average degree of ethoxylation of 16. The alcohol used here is Carbowax 750® (trademark of Union Carbide).

Product data:

$\eta$  (100°C) = 293.4 mm<sup>2</sup>/s

$\eta$  (40°C) = 3 999.0 mm<sup>2</sup>/s.

VIB = 217

Pour point = -22.1°C

$\bar{M}_w$ ,  $\bar{M}_n$  cannot be determined via GPC because of high absorption.

Yield about 100%

Example 16

As in Example 5, but instead of isodecyl methacrylate, C12-C15-alkyl methacrylate with 90% iso-content is used.

Product data:

$\eta$  (100°C) = 41.8 mm<sup>2</sup>/s

$\eta$  (40°C) = 417.6 mm<sup>2</sup>/s.

VIB 152

Pour point = -44.1°C

$\bar{M}_w$  = 3 430

$\bar{M}_n$  = 1 830

U = 0.78

Example 17

As in Example 1, but methacrylate component is C12-C15 alkyl methacrylate (90% iso), AMA/decene-ratio: 1 : 0.5

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mol, AMA fed in for 1 hour.

Product data:

$\eta$  (100°C) = 234.4 mm<sup>2</sup>/s

5  $\eta$  (40°C) = 4 810.6 mm<sup>2</sup>/s.

VIB = 165

Pour point = -25.6°C

$\bar{M}_w$  = 23 100

$\bar{M}_n$  = 3 230

10 U = 6.14

Practical Examples

Example 18

15

Comparing the viscosity data of an oligomer/ester oil mixture with those of a poly- $\alpha$ -olefin/ester oil mixture.

|                   | 20% PAO 100 in<br>TMA-OD®-ester | 20% oligomer from<br>Example 17 in<br>TMA-OD®-ester |
|-------------------|---------------------------------|-----------------------------------------------------|
| 20 $\eta$ (100°C) | 6.68 mm <sup>2</sup> /s         | 7.70 mm <sup>2</sup> /s                             |
| VIB               | 193                             | 212                                                 |
| CCS (-30°C)       | 1 800 mPa s                     | 1 600 mPa s                                         |

25 It is clearly apparent that with cooligomers in the mixture a lower viscosity may be achieved at -30°C, despite the higher viscosity at 100°, thereby obtaining a better low-temperature behaviour.

Example 19

30

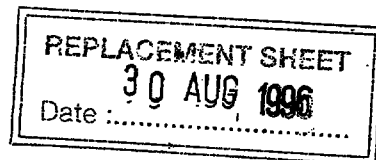
Comparing an oligomer/PAO formulation with a PAO6/PAO40 formulation when carrying out an MOT for a VW.

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|    | PAO40 in PAO 6 | Oligomer from<br>Example 18 in<br>PAO6 |
|----|----------------|----------------------------------------|
| 5  |                |                                        |
|    | Formulation    | 45% PAO 40                             |
|    |                | 14.2% commercially<br>available DI     |
| 10 | package        | 45% oligomer                           |
|    | 40.8% PAO6     | 14.2% commercially<br>available DI     |
|    | $\eta$ (100°C) | package                                |
|    | VI             | 40.8 PAO6                              |
|    | SAE-class      | 18.7 mm <sup>2</sup> /s                |
|    |                | 147                                    |
|    |                | 148                                    |
| 15 | VW-MOT result  | 10W-50                                 |
|    | 63.7 points,   | 10W-50                                 |
|    | rings free     | 67.2 points, all<br>rings free         |

Excellent diesel specifications can therefore be obtained with the oligomer/PAO mixture which results in good thermo-oxidative stability. It must also be noted that the pure polyalphaolefin formulation used for the purpose of comparison has an excellent diesel performance, as known.



Claims

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REPLACED

1. A process for preparing oligomers and cooligomers by means of radical polymerisation of at least one monomer component B) with a higher polymerisation tendency and 0 - 90 wt.% based on the oligomers of a monomer component A) with a lower polymerisation tendency, at an elevated temperature and in the presence of polymerisation initiators using a conventional polymerisation vessel, characterised in that
- a) a liquid phase comprising the monomer component A) or a solvent L or both is introduced to a polymerisation vessel, and is heated to the reaction temperature.
- b) the component B) with the higher polymerisation tendency is added, provided the component A) has been introduced, so that the molar ratio of the component B) to component A), passes through values of 0 to about 0.2 in the initial phase of polymerisation and reaches the value 0.2 to 20 in the final phase of polymerisation with the proviso that
- c) the reaction temperature is chosen within a range in which there is already a significant depolymerisation of a homopolymer comprising the more easily polymerisable monomer component B) and
- d) an initiator I is added throughout the entire polymerisation, initiator I being chosen such that the half-life periods at the relevant reaction temperature are 1 minute to about 5 hours, and the initiator amounts are 0.1 to 10 wt.% based on the total amount of monomers.
2. A process according to claim 1, characterised in

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that A) the Q-values (according to Alfrey-Price) of the monomers A) with the lower polymerisation tendency differ from those of the monomers B) with the higher polymerisation tendency by a factor  $\geq 5$ .

5

3. A process according to claims 1 and 2, characterised in that the range in which there is already a significant depolymerisation of a homopolymer comprising component B) is a range in which 3 - 80 wt.% of monomers (based on the sum of monomers + polymer) are registered under monomer/polymer equilibrium conditions.

10

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PROCESS FOR PREPARING HOMOLIGOMERS AND COOLIGOMERS

Abstract

- 5 A process for preparing oligomers and cooligomers via radical polymerisation of more polymerisable monomer component(s) B) and 0 - 90 wt.% (based on the oligomers) of a less polymerisable monomer component A), in which
- 10 a) a liquid phase comprising A) and/or a solvent is introduced into a conventional polymerisation vessel and heated to the reaction temperature,
- 15 b) B) is added after A), so that the molar ratio between B) and A) changes from 0 to about 0.2 in the initial polymerisation phase and reaches 0.2 to 20 in the final polymerisation phase, with the provisos that
- 20 c) the reaction temperature is such that there is significant depolymerisation of a homopolymer comprising B), and
- 25 d) 0.1 to 10 wt.% amounts (based on the monomers) of an initiator with half-life periods of 1 minute to about 5 hours at the reaction temperature, is added throughout the entire polymerisation.

5-00000000



### Claims

1. A process for preparing oligomers and cooligomers by means of radical polymerisation of at least one monomer component B) with a higher polymerisation tendency and 0 - 90 wt.% based on the oligomers of a monomer component A) with a lower polymerisation tendency, at an elevated temperature and in the presence of polymerisation initiators using a conventional polymerisation vessel, characterised in that

the Q-values, according to Alfrey Price, of the monomers A) with the lower polymerisation tendency and of the monomers B) with the higher polymerisation tendency differ from one another by a factor  $\geq 5$  and that

- a) a liquid phase comprising the monomer component A) or a solvent L or both is introduced to a polymerisation vessel, and is heated to the reaction temperature,
- b) the component B) with the higher polymerisation tendency is added, provided the component A) has been introduced, so that the molar ratio of the component B) to component A), passes through values of 0 to about 0.2 in the initial phase of polymerisation and reaches the value 0.2 to 20 in the final phase of polymerisation with the proviso that
- c) the reaction temperature is chosen within a range in which a homopolymer of the more easily polymerisable monomer component B) depolymerises to such an extent that 3 - 80 wt.% of monomers (based on the sum of monomers plus polymer) are recorded under monomer/polymer equilibrium conditions.



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- d) the initiator I is added throughout the entire polymerisation, initiator I being chosen such that the half-life periods at the relevant reaction temperature are 1 minute to about 5 hours, and the initiator amounts are 0.1 to 10 wt.% based on the total amount of monomers.