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Novel peroxide monomer and a polymer therefrom.

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Proprietor: Nippon Paint Co., Ltd.
2-1-2, Oyodokita Oyodo-ku
Osaka-shi Osaka-fu(JP)

Inventor: Tsuboniwa, Noriyuki
2-26-21, Arakawa
Higashiosaka-shi Osaka-fu(JP)
Inventor: Urano, Satoshi
6A36-301, Otokoyamakoro
Yawata-shi Kyoto-fu(JP)
Inventor: Mizuguchi, Ryuzo
42-6, Hashimotokurigatani
Yawata-shi Kyoto-fu(JP)

Representative: Perry, Robert Edward et al
GILL JENNINGS & EVERY 53-64 Chancery
Lane
London WC2A 1HN(GB)

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Description

The present invention relates to a novel peroxide having a polymerisable double bond and to a polymer obtained therefrom.

Background of the Invention

Compounds which have both a polymerisable double bond and a peroxide group are known, i.e. allylperoxy carbonates of the formula

\[ \text{CH}_2 = \text{CR-CH}_2 - \text{O-CO-O-CO-R}^1 \]

wherein \( R^1 \) is alkyl or cycloalkyl and \( R \) is hydrogen or alkyl. However, the allyl group has poor homo- and copolymerisability.

US-A-3853937 discloses organic peroxides of the formula

\[ \text{CH}_2 = \text{CR-NR}^2 - \text{CO-OO-R}^3 \]

wherein \( R \) is H or methyl, \( R^2 \) is alkyl, cycloalkyl, aralkyl or aryl, and \( R^3 \) is tertiary alkyl, cycloalkyl or di- or tertiary alkylene. The peroxides are used for the production of polymers containing isocyanate groups which may be cross-linked.

GB-A-1184618 discloses peroxycarbonic acid esters, which are prepared by reacting an isocyanate with a peroxide in an inert solvent.

Summary of the Invention

Novel peroxide monomers according to the present invention have the formula

\[ \text{CH}_2 = \text{CR-A-NH-CO-OO-B} \]

wherein \( R \) is H or \( C_1 - C_5 \) alkyl; A is a bond, \(-\text{CO-}\) or \(-\text{CO-O-CH}_2\text{CH}_2\text{-}\); and \( B \) is derived from a hydroperoxide of the formula \( \text{B-OOH} \).

In another aspect of the invention, a novel polymer, having a molecular weight of 1,000 to 100,000 whose main chain is composed of carbon-carbon bonds, has a pendant peroxide group of the formula

\[ -\text{A-NH-CO-OO-B} \]

wherein \( A \) and \( B \) are as defined above, the content of the pendant peroxide group being 0.1 to 99.99% by weight.

Detailed Description of the Invention

The peroxide monomer can be prepared by reacting a hydroperoxide with an isocyanate compound of the formula:

\[ \text{CH}_2 = \text{CR-NCO} \quad (\text{III}) \]

\[ \text{CH}_2 = \text{CR-CO-NCO} \quad (\text{IV}) \]

\[ \text{CH}_2 = \text{CR-CO-O-CH}_2\text{CH}_2\text{-NCO} \quad (\text{V}) \]

wherein \( R \) is the same as mentioned above.

The isocyanate compounds (III) to (V) are known. The compound (III) may be prepared by, for example, a process described in Angew. Chem. Int. Ed. Engl. 18(1979) No.4. The compound (IV) may be prepared by a process disclosed in Japanese Patent Publication (unexamined) 115557/1985, or a process from an intermediate shown in Die Makromolekule Chemie, 131, (1970), 247-257 (No.3199). Also, United Kingdom Patent 1,252,099 discloses one process for preparing the isocyanate compound (V).

The hydroperoxide employed in the reaction is a hydrogen peroxide of which one hydrogen is substituted for an alkyl group or another organic atom group. Examples of the hydroperoxides are t-butyl
hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-mentane hydroperoxide, per-
acetic acid, 2,5-dimethyl-2,5-dihydroperoxyhexane, 2,5-dimethyl-2,5-dihydroperoxyhexane-3 and the like.
The hydroperoxide can be available in the form of a concentrated or diluted solution. If it is obtained in the
form of an aqueous solution, water may be substituted for an organic solvent by, for example, extraction.
Also, the aqueous hydroperoxide solution may be employed intact, but an undesired by-product, such as an
amide, may be produced.
A reaction of the isocyanate compound with the hydroperoxide can be carried out in an inert solvent, if
desired. The inert solvent is one that does not adversely affect the reaction per se, including an aliphatic
hydrocarbon, such as pentane, hexane, heptane and the like; an aromatic hydrocarbon, such as benzene,
toluene, xylene and the like; a cyclohydrocarbon, such as cyclohexane, methylcyclohexane, decaline, and
the like; a hydrocarbon type solvent, such as petroleum ether, petroleum benzine and the like; a
halogenated hydrocarbon, such as carbon tetrachloride, chloroform, 1,2-dichloroethane and the like; an
ether, such as ethyl ether, isopropyl ether, anisole, dioxane, tetrahydrofuran, and the like; a ketone, such as
acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, acetophenone, isophorone and the
like; an ester, such as ethyl acetate, butyl acetate and the like; acetonitrile; dimethylformamide; dimethylox-
oxide; and the like. The reaction can be carried out at a temperature at which the hydroperoxide is not
decomposed, for example -20 to 10 °C. If a temperature is over 10 °C, the hydroperoxide would have a
risk to decompose. If the temperature is too low, the reaction rate decreases. A catalyst may be used in the
reaction, but generally no catalyst is needed in this reaction.
If necessary, a polymerization inhibitor may be added in the reaction system to prevent unnecessary
polymerization on terminal double bonds. Examples of the polymerization inhibitors are hydroquinone, p-
methoxyphenol, 2,6-di-t-butyl-4-methylphenol, 4-t-butylcatechol, bisdihydroxybenzylbenzene, 2,2'-
methylenebis(6-t-butyl-3-methylphenol), 4,4'-butylidene(6-t-butyl-3-methylphenol), 4,4'-thiobis(6-t-butyl-3-
methylphenol), p-nitroso phenol, diisopropylxantogensulfide, N-nitroso-phenyldihydrxylamine ammonium salt,
1,1-diphenyl-2-picrylhydrazine, 1,3,5-triphenylpheldazyl, 2,6-di-t-butyl-alpha-(3,5-di-butyl-4-oxo-2,5-
cyclohexadiene-1-lydene)-p-trioly, 2,2,6,6-tetramethyl-4-piperidine-1-ox, dithiobenzylsulfide, p,p'-ditolyl-
trisulfide, p,p'-ditolyltrisulfide, dibenzyltetrasulfide, tetraethylthiuramsulfide and the like.
The reaction can be carried out by adding the hydroperoxide to the isocyanate compound (III-IV), vice
versa. Termination of the reaction can be identified by disappearance of an absorption of isocyanate groups
in infrared spectrum.
The obtained peroxide monomer can be isolated, but can be employed intact. The obtained peroxide
monomer has the following structure:
The portion a of the above chemical structure shows a double bond which is incorporated into a polymer backbone to form a polymer having a pendant peroxide group. The portion b produces

\[ \text{H} \]

\[ \text{-N} \cdot \]

after decomposing the portion c by heat and decarboxylation, and is reacted with another functional group to be able to form a graft resin. The portion c is radically decomposed by heat to act as an initiator. Accordingly, the peroxide monomer of the present invention acts as a radical initiator and then forms itself a polymer chain as a monomer.

The pendant peroxide group-containing polymer of the present invention can be prepared by two processes. The first process is that the peroxide monomer obtained in the present invention is polymerized alone or copolymerized with another polymerizable monomer. The second one is that the isocyanate monomer (III), (IV) or (V) is polymerized alone or copolymerized with another monomer to obtain a polymer having isocyanate groups which are then reacted with the hydroperoxide.

The first process will be explained. In copolymerization, a monomer to be copolymerized with the peroxide monomer can be classified for convenience into an active hydrogen containing-ethylenically unsaturated compound and an ethylenically unsaturated compound not containing an active hydrogen.

Examples of the active hydrogen containing-ethylenically unsaturated compounds are unsaturated acids, such as acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, 2-isopropylacrylic acid, trans (cis)-2-decenoic acid, alpha-chloroacrylic acid, beta-transnitroacrylic acid and the like; unsaturated alcohols, such as crotonic alcohol, cinnamyl alcohol, o-hydroxyxystrene, an monoester of a glycol (such as ethylene glycol, propylene glycol) and the above mentioned unsaturated acids, and the like; unsaturated amides, such as amides of the above listed unsaturated acids, for example acrylamide, methacrylamide, crotonamidine, cinnamamide, p-benzamidestereene and the like; unsaturated sulfonic acids and a salt thereof, such as 2-sulfoethyl acrylate, 2-sulfoethyl methacrylate, t-butylacrylamide sulfonic acid, 4-sulfophenyl acrylate, p-vinylbenzene sulfonic acid, and the like; unsaturated phosphoric acid, for example acid phosphoxyethylmethacrylate, 3-chloro-2-amidophosphoxypropyl methacrylate, acid phosphoxypropyl methacrylate, vinyl phosphate, isopropeny1 phosphate and the like; unsaturate amines, such as allylamine, o-aminostyrene, m-aminostyrene, t-butilaminoethyl methacrylate, 7-amino-3,7-dimethyloctyl acrylate and the like. These are employed alone or in combination.

Examples of the ethylenically unsaturated compounds not having an active hydrogen are monooolefin and diolefin hydrocarbons, such as styrene, alpha-methylstyrene, ethylene, propylene, butylene, amylene, xylene, butadiene-1,3, isoprene and the like; halogenated monooolefin and diolefin hydrocarbons, such as alpha-chlorostyrene, 2,5-dibromostyrene, 3,4-dichlorostyrene, o-, m- and p-fluorostyrene, 2,6-dichlorostyrene, 3-fluoro-4-chlorostyrene, 3-chloro-4-fluorostyrene, 2,4,5-trichlorostyrene, 2-chlorohexene, 2-bromohexene, 2-iodopentene, cis- and trans-1,2-dichloroethylene, 1,2-dibromoethylene, 1,2-difluoroethylene, 1,2-diodoethylene, chloroethylene(vinyl chloride), 1,1-dichloroethylene(vinylidene chloride), 1,1-dibromoethylene, 1,1,2-trifluoroethylene, chlorobutadiene and other halogenated olefin compounds; organic and inorganic esters, such as vinyl acetate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl benzoate, vinyl halobenzoate, vinyl-p-methoxybenzoate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, hexyl (meth)acrylate, methyl crotonate and ethyl tiglate, isopropenyl acetate, isopropenyl butyrate, isopropenyl valerate, isopropenyl caproate, isopropenyl benzoate, isopropenyl-p-chlorobenzoate, vinyl-alpha-chlorooacetate, vinyl-alpha-bromovalerate and the like; esters derived from alkenyl alcohols, such as allyl chloride, allyl cyanide, allyl chloride carbonate, allyl nitrate, allyl thiocyanate, allyl formate, allyl acetate, acetate propionate, allyl butyrate, allyl crotonate, allyl aminocetate, allyl acetoacetate, allyl thioacetate, beta-ethylallyl alcohol, beta-propyallyl alcohol and the like; organic nitriles, such as acrylonitrile, methacrylonitrile, ethacrylonitrile, 3-octenenitrile, crotononitrile, oleonitrile and the like.

Polymerization or copolymerization is generally carried out in the presence of a polymerization initiator in a solvent which is inactive with the polymerization. The polymerization initiator is preferably a radical initiator, such as azobisisobutyronitrile, bezoyl peroxide, cumene peroxide, tetramethylthiuram disulfide, 2,2’-azobis(4-methoxy-2,4-dimethylvaleronitrile), acetylclohexylsulfonyl peroxide, 2,2-azobis(2,4-dimethylvaleronitrile) and the like. The polymerization initiator can be used in an amount of 0.1 to 10 % by weight based on a monomer weight. Examples of the solvents are the above mentioned inert solvents, alcohols or a mixture thereof. Polymerization may be carried out at a temperature of 40 to 150 °C, preferably 40 to 80
In the second process, since the isocyanate compound is used uncapped or unblocked, a compound reactive with an isocyanate group can not be employed in the polymerization reaction and the reaction with the hydroperoxide. Accordingly, a solvent which contains an active hydrogen can not be employed and a monomer which contains an active hydrogen also can not be used.

The reaction of the polymer in the second process with the hydroperoxide may be conducted with equal molar ratio so that all isocyanate groups are consumed for the hydroperoxide. Also, the hydroperoxide may be used in a less molar amount than the isocyanate groups to leave a part of the isocyanate groups for further reactions. The remained isocyanate groups may be reacted with other active hydrogen containing-compounds, whereby other functional groups can be incorporated into the polymer. Examples of the other active hydrogen containing-compounds are alcohols, phenols, active methylenes, lactams, N-hydroxyimides, oximes, imidazoles, triazoles and amines. Also, a fluorine-containing compound, a melamine derivative, a spiro compound, an Si group containing compound, a glycidol, a photocrosslinkable compound or a ultraviolet absorbent may be reacted to be coexistent with the peroxide groups. It may also be reacted with an active hydrogen containing ethylenically unsaturated compound to introduce polymerizable double bonds.

The polymer of the present invention schemetically shows as follow.

\[
\begin{align*}
&\text{NH–C–O–O–B} \\
&\text{||} \\
&\text{O} \\
&\text{|--(P) if exist}
\end{align*}
\]

It is understandable from the above chemical structure that the polymer of the present invention has a radical initiating ability at a portion which has been decomposed by heat to form a graft polymer. In the structure, P shows the other pendant groups. If P is an ethylenically unsaturated group, the polymer has both an unsaturated group and a peroxide group so as to be able to cure without externally adding a curing agent.

In the first process for preparing the polymer, an isocyanate group is already blocked so as to freely select a solvent or another monomer. Also, it is not needed to consider gelation with water during polymerizing.

In the second process, it is not necessary to take care to a decomposing temperature of the peroxide, so that a conventional radical polymerization can be employed. There also would be few decomposing loss of the hydroperoxide.

Examples

The present invention is illustrated by the following examples.

Example 1

An adduct of methacryloyl isocyanate and cumene hydroperoxide

Methacryloyl isocyanate (1.10 g; 10 mmol) and dichloroethane (20 g) were mixed and cooled to 0 to 2 °C. A mixture of a 73 % cumene hydroperoxide solution in a hydrocarbon (21.0 g; 10 mmol) with dichloroethane (20 g) was added dropwise for about 5 minutes and mixing was continued for one hour. After it was identified that an absorption of NCO by infrared spectrum disappeared, a small amount of solvent was removed by an evaporator to obtain a 5 % product solution in dichloroethane which has a viscosity Cp of 1.5 (25 °C, EL type viscometer).

Example 2

An adduct of methacryloyl isocyanate and t-butyl hydroperoxide
Methacryloyl isocyanate (1.42 g; 12.8 mmol) was dissolved in dichloroethane (5 g) and cooled to 0 °C. A 14 % dichloroethane solution (8.2 g; 12.8 mmol) of t-butyl hydroperoxide was added dropwise for about 30 minutes and mixing was continued for about one hour. The 14 % dichloroethane solution of t-butyl hydroperoxide was prepared by extracting an 80 % t-butyl hydroperoxide aqueous solution with dichloroethane and then drying with magnesium sulfate followed by identifying a content by NMR. After it was identified that an absorption of NCO by infrared spectrum disappeared, dichloroethane was removed at a low temperature by an evaporator and dried by a vacuum pump to obtain white solid having a melting point of 55 to 60 °C and a decomposing point of 115 to 120 °C.

Example 3

An adduct of isocyanatoethyl methacrylate and t-butyl hydroperoxide

Isocyanatoethyl methacrylate (1.55 g; 10 mmol) was dissolved in dichloroethane (5 g) and cooled to 0 °C. A 18 % dichloroethane solution (9.0 g; 10 mmol) of t-butyl hydroperoxide was added dropwise for about 10 minutes. Triethylamine (20 mg; 0.018 mol%) was then added and mixing was continued for about one hour. After it was identified that an absorption of NCO by infrared spectrum disappeared, it was concentrated under a reduced pressure by a vacuum pump to obtain an oil product having a viscosity (Cp) of 127.6 (25 °C, EL type viscometer).

Example 4

A copolymer having an acrylisocyanate blocked by t-butyl hydroperoxide

Methacryloylisocyanate (2.2 g; 20 mmol) and butyl acetate (2.0 g) were cooled 15 to 20 °C and a 20 % toluene solution (6.0 g; 20 mmol) of t-butyl hydroperoxide was added dropwise for 5 minutes. The toluene solution of t-butyl hydroperoxide was prepared by extracting several times an 80 % t-butyl hydroperoxide aqueous solution with toluene and then drying with magnesium sulfate followed by identifying a content by NMR. After it was identified that an absorption of NCO by infrared spectrum disappeared and that an absorption of the adduct exists at 1,800 cm⁻¹, n-butyl acrylate (4.4 g) and methyl methacrylate (2.0 g) were added and mixed at 80 °C. Next, 2,2'-azobis(2,4-dimethyl)valeronitrile (available from Wako pure Chemical Industries, LTD. as V-65) (3 %; 300 mg) was dissolved in butyl acetate (5.0 g), which was added to the mixture obtained above for about 30 minutes. It was aged for one hour to obtain a copolymer having a number average molecular weight of 1,590 and a conversion of 61 %.

Example 5

A copolymer having a pendant acrylisocyanate blocked by t-butyl hydroperoxide

Methacryloyl isocyanate (1.7 g; 15 mmol), n-butyl acrylate (4.0 g), styrene (2.0 g) and 2,2'-azobis(2,4-dimethyl)valeronitrile (V-65) (231 mg; 3 %) were mixed and added dropwise to butyl acetate (10.0 g) at 110 °C for one hour. At 110 °C, the resultant mixture was aged for 2 hours and cooled to 0 to 5 °C, to which a mixture of a 50 % benzene solution (2.7 g) of t-butyl hydroperoxide with butyl acetate 4.2 g added dropwise for 10 minutes and continued to mix. The benzene solution of t-butyl hydroperoxide was prepared by extracting several times a t-butyl hydroperoxide aqueous solution with benzene and then drying with magnesium sulfate followed by identifying a content by NMR. It was identified that an absorption of NCO by infrared spectrum disappeared. An objective resin was obtained with a conversion of 80 % and a number average molecular weight of 6,300.

Example 6

A copolymer having a pendant acrylisocyanate blocked by cumene hydroperoxide

Methacryloyl isocyanate (2.8 g; 25 mmol), n-butyl acrylate (8.0 g), styrene (4.0 g) and 2,2'-azobis(2,4-dimethyl)valeronitrile (V-65) (444 mg; 3 %) were mixed and added dropwise to butyl acetate (15.0 g) at 110 °C for one hour. At 110 °C, the resultant mixture was aged for 2 hours and cooled to 0 to 5 °C, to which a mixture of a 73 % cumene hydroperoxide solution (5.2 g) with butyl acetate (1.0 g) was added dropwise for about 5 minutes and continued to mix for one hour. It was identified that an absorption of NCO by infrared
spectrum disappeared. An objective resin was obtained with a conversion of 80% and a number average molecular weight of 7,200.

Example 7

A copolymer having a pendent isocyanate blocked by t-butyl hydroperoxide

Isocyanatoethyl methacrylate (1.6 g; 10 mmol), butyl acrylate (4.0 g), styrene (1.5 g) and 2,2'-azobis (2,4-dimethyl)valeronitrile (V-65) (220 mg; 3%) were mixed and added dropwise to butyl acetate (11.3 g) at 100 °C for one hour. At 100 °C, the resultant mixture was aged for one hour and cooled to 0 °C, to which a mixture of a 50% benzene solution (1.8 g; 10.0 mmol) of t-butyl hydroperoxide with butyl acetate (4.5 g) was added dropwise for 30 minutes and continued to mix. Then, dibutyltin dilaurate (20 mg) was added and mixed at room temperature for one day. It was identified that an absorption of NCO by infrared spectrum disappeared. An objective resin was obtained with a conversion of 78% and a number average molecular weight of 7,700.

Example 8

A copolymer having a pendant acylisocyanate blocked by t-butyl hydroperoxide and a double bond

Methacryloyl isocyanate (3.1 g; 28 mmol), n-butyl acrylate (4.7 g), methyl acrylate (3.4 g) and 2,2'-azobis(2,4-dimethyl)valeronitrile (V-65) (300 mg; 3%) were mixed and added dropwise to butyl acetate (17.0 g) at 85 °C for one hour. The resultant mixture was aged for one hour and cooled to 10 °C, to which a mixture of 2-hydroxyethyl methacrylate (2.0 g; 15.6 mmol) with butyl acetate (1.0 g) was added dropwise. Next, (8.0 g; 12.4 mmol) of a dichloroethane solution containing t-butyl hydroperoxide at a concentration of 14% was diluted with butyl acetate (16 g) and added dropwise. The dichloroethane solution of t-butyl hydroperoxide was prepared by extracting several times a t-butyl hydroperoxide aqueous solution with dichloroethane and then drying with magnesium sulfate followed by identifying a content by NMR. It was identified that an absorption of NCO by infrared spectrum disappeared. An objective resin was obtained with a conversion of 75% and a number average molecular weight of 8,800.

Example 9

A copolymer having acylisocyanates, a part of which is blocked by t-butyl hydroperoxide and the other part of which is blocked by phenol

Methacryloyl isocyanate (3.1 g; 28 mmol), n-butyl acrylate (4.7 g), methyl methacrylate (3.4 g) and 2,2'-azobis(2,4-dimethyl)valeronitrile (V-65) (300 mg; 3%) were mixed and added dropwise to butyl acetate (17.0 g) at 85 °C for one hour. At 85 °C, the resultant mixture was aged for 1 hour and cooled to 10 °C, to which a mixture of phenol (1.47 g; 15.6 mmol) with butyl acetate (1 g) was added dropwise. Then, it was aged for one hour and a mixture of a 14% dichloroethane solution (8.0 g; 12.4 mmol) of t-butyl hydroperoxide with butyl acetate (16 g) was added dropwise. The dichloroethane solution of t-butyl hydroperoxide was prepared by extracting several times a t-butyl hydroperoxide aqueous solution with dichloroethane and then drying with magnesium sulfate followed by identifying a content by NMR. After completion of addition, mixing was continued for 30 minutes. It was identified that an absorption of NCO by infrared spectrum disappeared. An objective resin was obtained with a conversion of 70% and a number average molecular weight of 8,500.

Hexane was added to each copolymer obtained in Examples 1 to 6 and to take a solid portion which was washed several times with hexane to obtain a sample. The sample was mixed with ethylene glycol dimethacrylate and n-butyl acrylate and heated to 120 °C to observe gelation due to radical polymerization.

Hexane was added to the copolymer of Example 5 to take out a solid portion which was then washed several times with hexane to obtain a sample. The sample was dissolved in butyl acetate and heated to 120 °C to observe gelation due to radical polymerization.

Claims

1. A compound having the formula
CH₂ = CR-A-NH-CO-OO-B  (I)

wherein R is H or C₁₋₅ alkyl; A is a bond, -CO- or -CO-O-CH₂CH₂-; and B is derived from a hydroperoxide of the formula B-OOH.

2. A process for preparing a compound of claim 1, comprising reacting the hydroperoxide defined in claim 1 with an isocyanate compound having the formula

CH₂ = CR-A-NCO

wherein A and R are as defined in claim 1.

3. A process according to claim 2, wherein the reaction is carried out in an inert solvent.

4. A polymer having a molecular weight of 1,000 to 100,000, whose main chain is composed of carbon-carbon bonds, and which has a pendant peroxide group of the formula

-A-NH-CO-OO-B  (II)

wherein A and B are as defined in claim 1, the content of the pendant peroxide group being 0.1 to 99.9% by weight.

5. A polymer according to claim 4, which further contains a polymerisable double bond.

6. A process for preparing a polymer of claim 4, comprising polymerising a compound of claim 1, alone or with one or more other polymerisable monomers.

7. A process for preparing a polymer of claim 4, comprising polymerising an isocyanate compound as defined in claim 2, alone or with one or more other polymerisable monomers, and reacting the resultant polymer (containing an isocyanate group) with a hydroperoxide.

8. A process according to claim 7, wherein the hydroperoxide and an active hydrogen-containing polymerisable monomer are simultaneously reacted with the isocyanate group-containing polymer, to incorporate a polymerisable double bond in the product.

9. A process according to any of claims 6 to 8, wherein the polymerisation is carried out in an inert solvent.

Patentansprüche

1. Verbindung der Formel

CH₂ = CR-A-NH-CO-OO-B  (I)

wärin R H oder C₁₋₅-Alkyl ist; A ist eine Bindung, -CO- oder -CO-O-CH₂CH₂-; und B stammt von einem Hydroperoxid der Formel B-OOH.

2. Verfahren zur Herstellung einer Verbindung gemäß Anspruch 1, umfassend das Umsetzen des in Anspruch 1 definierten Hydroperoxides mit einer Isocyanatverbindung der Formel

CH₂ = CR-A-NCO

wobei A und R wie in Anspruch 1 definiert sind.

3. Verfahren gemäß Anspruch 2, wobei die Reaktion in einem inerten Lösungsmittel ausgeführt wird.

4. Polymer mit einem Molekulargewicht von 1000 bis 100,000, dessen Hauptkette aus Kohlenstoff-Kohlenstoff-Bindungen besteht und das eine anhäuhrende Peroxidgruppe der Formel
hat, wobei A und B wie in Anspruch 1 definiert sind und der Gehalt an anhängender Peroxidgruppe 0,1 bis 99,9 Gew.% beträgt.

5. Polymer gemäß Anspruch 4, das ausserdem eine polymerisierbare Doppelbindung enthält.

6. Verfahren zur Herstellung eines Polymeren gemäß Anspruch 4, das die Polymerisation einer Verbin-
dung gemäß Anspruch 1 umfasst, alleine oder mit einem oder mehreren anderen, polymerisierbaren
Monomeren.

7. Verfahren zur Herstellung eines Polymeren gemäß Anspruch 4, das die Polymerisation einer Isocyan-
aterbindung, wie sie in Anspruch 2 definiert ist, alleine oder mit einem oder mehreren anderen
polymerisierbaren Monomeren, und Reaktion des resultierenden Polymeren (enthaltend eine Isocyanat-
gruppe) mit einem Hydroperoxid umfasst.

8. Verfahren gemäß Anspruch 7, wobei das Hydroperoxid und ein polymerisierbares Monomer mit
aktivem Wasserstoff gleichzeitig mit dem Isocyanatgruppen enthaltenden Polymer umgesetzt werden,
wodurch eine polymerisierbare Doppelbindung in das Produkt eingeführt wird.

9. Verfahren gemäß einem der Ansprüche 6 bis 8, wobei die Polymerisation in einem inerten Lösungs-
mittel durchgeführt wird.

Revendications

1. Un composé répondant à la formule :

\[ \text{CH}_2 = \text{CR-A-NH-CO-OO-B} \quad (I) \]

dans laquelle R est H ou un groupe alkyle en C\textsubscript{1}-C\textsubscript{3} ; A est une liaison ou un groupe -CO- ou -CO-O-
CH\textsubscript{2}CH\textsubscript{2}- ; et B est dérivé d’un hydroperoxyde de formule B-OOH.

2. Un procédé pour préparer un composé selon la revendication 1, comprenant la réaction de l’hydroper-
oxyde défini à la revendication 1 avec un isocyanate répondant à la formule :

\[ \text{CH}_2 = \text{CR-A-NCO} \]

dans laquelle A et R sont tels que définis dans la revendication 1.

3. Un procédé selon la revendication 2, dans lequel la réaction est mise en œuvre dans un solvant inerte.

4. Un polymère ayant un poids moléculaire de 1 000 à 100 000, dont la chaîne principale est composée
de liaisons carbone-carbone et qui a des groupes peroxydes pendants de formule :

\[ -\text{A-NH-CO-OO-B} \quad (II) \]

dans laquelle A et B sont tels que définis à la revendication 1, la teneur en groupes peroxydes pendants étant de 0,1 à 99,9 % en poids.

5. Un polymère selon la revendication 4, qui contient en outre des doubles liaisons polymérisables.

6. Un procédé pour préparer un polymère selon la revendication 4, comprenant la polymérisation d’un
composé selon la revendication 1, seul ou avec un ou plusieurs autres monomères polymérisables.

7. Un procédé pour préparer un polymère selon la revendication 4, comprenant la polymérisation d’un
isocyanate tel que défini à la revendication 2, seul ou avec un ou plusieurs autres monomères
polymérisables et la réaction du polymère résultant (contenant des groupes isocyanates) avec un
hydroperoxyde.

8. Un procédé selon la revendication 7, dans lequel l'hydroperoxyde et un monomère polymérisable contenant un hydrogène actif sont mis à réagir simultanément avec le polymère contenant des groupes isocyanates pour incorporer des doubles liaisons polymérisables dans le produit.

9. Un procédé selon l'une quelconque des revendications 6 à 8, dans lequel la polymérisation est mise en œuvre dans un solvant inerte.