

Polymeric Biocide

The present invention relates to novel polymers that contain algicidal groups and to compositions containing said polymers. The invention further relates to a process for the preparation of these novel compounds and to the use thereof as algicides.

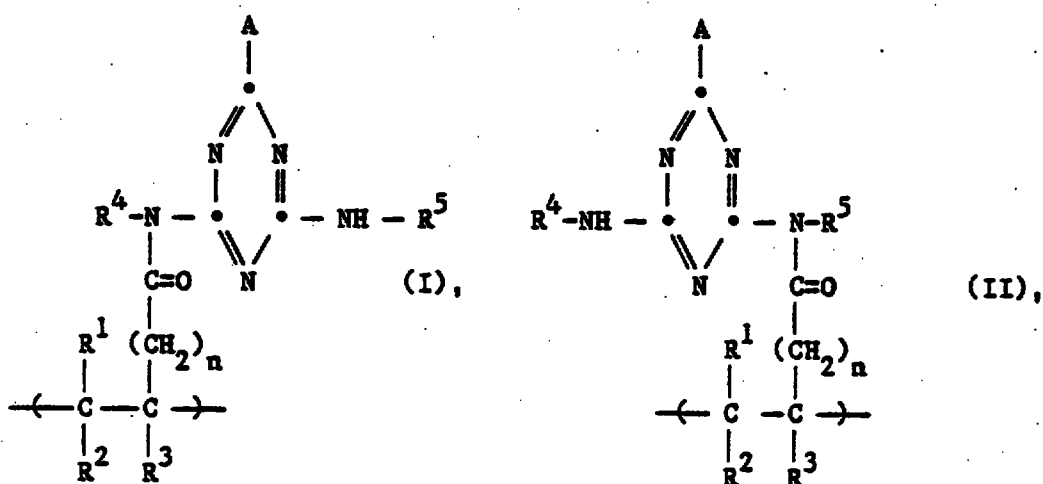
The principle of attaching a biocidal group to a polymer is known. Thus, for example, US patent specification 3,167,473 describes polymers in which organotin groups in esterified form are attached to a polymer.

In J. Coatings Techn., 48, 31 (1976), Pittman et al. describe a monoamino-s-triazine which, coupled through an amide group, has been incorporated into a polyacrylate.

Specific 2,6-diamino-s-triazines as particularly effective sea water algicides are known from EP patent 3749. It would be desirable to attach these compounds also to a polymer in order to improve their compatibility with other substrate components and, in particular, to diminish their tendency to recrystallise in paint formulations. As two amino groups are present in the active ingredient molecule, crosslinking must be expected to occur when incorporating these compounds into a polymer that contains carboxyl groups, and that consequently compatibility with other paint components or the water-solubility of the functionalised polymer will be reduced. Attachment of both amino groups of the diaminotriazines to the polymer would furthermore result in the liberation of the biocidal triazine by hydrolytic cleavage of the amide bond being retarded in comparison with the attachment of active groups by single amino groups, and that therefore the effective concentration of free biocidal diaminotriazine will consequently fall.

Surprisingly, it has now been found that specific diamino-s-triazines which carry at least one voluminous group at an amino nitrogen atom can be attached to a carboxylic acid or to a reactive derivative thereof only with one amino group, whereby no crosslinking occurs in the functionalised polymer. It is also surprising that, even at high triazine concentrations, the good compatability of the functionalised polymer with other paint components is retained. It is thereby possible to use high concentrations of active ingredient.

The present invention relates to organic polymers having a molecular weight from 1,000 to 150,000 and containing the structural unit of the formula I and/or of the formula II



wherein R^1 is hydrogen, R^2 is hydrogen or $-COOR^7$ and R^3 is hydrogen or methyl, and R^1 additionally is methyl if R^2 is $-COOR^7$ and if R^3 is methyl, and wherein R^2 additionally is methyl if R^1 and R^3 are hydrogen; n is 0 or, if R^1 , R^2 and R^3 are hydrogen, is 1; R^4 is straight chain C_2 - C_6 alkyl or C_3 - C_6 cycloalkyl; R^5 is branched C_3 - C_6 alkyl; A is $-SR^6$, $-OR^6$ or $-Cl$, in which R^6 is C_1 - C_3 alkyl; R^7 is hydrogen, C_1 - C_{20} alkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, phenyl, C_5 - C_{12} cycloalkyl, C_7 - C_{14} aralkyl, C_7 - C_{14} alkaryl, C_2 - C_{20} alkyl which is substituted by one or two hydroxyl groups or is C_3 - C_{20} alkyl which is interrupted by 1 to 5 identical or different members selected from $-O-$, $-S-$ and $-N(CH_3)-$, and is unsubstituted or substituted by a

hydroxyl group, with the proviso that any recurring hetero atoms must be separated by at least one methylene group; or the copolymers thereof with at least one compound which contains a polymerisable double bond, such that the molar ratio of the component or components of the formula I and/or of the formula II to the comonomer component may be up to 0.5:99.5.

R^4 as straight chain C_2-C_6 alkyl may be ethyl, n-propyl, n-butyl, n-pentyl or n-hexyl, with ethyl being preferred. R^4 as C_3-C_6 cycloalkyl may be cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, with cyclopropyl being especially preferred.

R^5 as branched C_3-C_6 alkyl may be isopropyl, sec-butyl, tert-butyl, 1,2-dimethylpropyl, 1,3-dimethylpropyl, 2,3-dimethylpropyl, tert-pentyl, sec-hexyl or tert-hexyl. Isopropyl, tert-butyl or 1,2-dimethylpropyl is preferred, with tert-butyl being especially preferred.

R^6 as C_1-C_3 alkyl is methyl, ethyl, n-propyl or isopropyl, with methyl being preferred. A is $-SR^6$, $-OR^6$ or $-Cl$, with $-SR^6$ or $-Cl$ being preferred; $-SR^6$ is particularly preferred, but the most preferred meaning is $-SCH_3$.

R^7 as C_1-C_{20} alkyl may be methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, 1,1-dimethylbutyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, 1,1,3,3-tetramethylbutyl, 1,1,3,3-tetramethylhexyl, n-undecyl, n-dodecyl, 1,1,3,3,5,5-hexamethylhexyl, n-tetradecyl, n-hexadecyl, n-octadecyl or n-eicosyl. The preferred meaning is methyl.

R^7 as C_2-C_{12} alkenyl may be vinyl, allyl, but-3-enyl, pent-4-enyl, hex-5-enyl, oct-7-enyl, dec-9-enyl or dodec-11-enyl. Vinyl or allyl is preferred. R^7 as C_2-C_{12} alkynyl may be ethynyl, propargyl, but-3-ynyl, hex-5-ynyl, oct-7-ynyl, dec-9-ynyl or dodec-11-ynyl, with propargyl being preferred.

R^7 as C_5-C_{12} cycloalkyl may be cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl or cyclododecyl. C_5-C_9 Cycloalkyl is preferred and cyclohexyl most preferred.

R^7 as C_7-C_{14} aralkyl may be benzyl, phenylethyl, α,α -dimethylbenzyl, phenylbutyl, phenyl- α,α -dimethylpropyl, phenylhexyl or phenyl- α,α -dimethylbutyl, phenyloctyl, or phenyl- α,α -dimethylhexyl, with benzyl being preferred.

R^7 as C_7-C_{14} alkaryl may be o-, m- or p-tolyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- or 3,6-dimethylphenyl, o-, m- or p-ethylphenyl, o-, m- or p-propylphenyl, o-, m- or p-isopropylphenyl, o-, m- or p-butylphenyl, o-, m- or p-sec-butylphenyl, o-, m- or p-tert-butylphenyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- or 3,6-dibutylphenyl or di-tert-butylphenyl, or o-, m- or p-hexylphenyl or o-, m- or p-octylphenyl. Preferred meanings are o-, m- or p-tolyl.

R^7 as C_2-C_{20} alkyl which is substituted by 1 or 2 hydroxyl groups may be 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl, 2-hydroxyhexyl, 2-hydroxyoctyl, 2-hydroxydecyl, 2-hydroxydodecyl, 2-hydroxytetradecyl, 2-hydroxyhexadecyl, 2-hydroxyoctadecyl, 2-hydroxyeicosyl or 2,3-dihydroxypropyl. R^7 is preferably C_2-C_{14} alkyl which is substituted by 1 or 2 hydroxyl groups and is most preferably 2-hydroxyethyl, 2-hydroxypropyl or 2,3-dihydroxypropyl.

R^7 as C_3-C_{20} alkyl which is interrupted by 1 to 5 members selected from -O-, -S- or -N(CH₃)- and is unsubstituted or substituted by a hydroxyl group may be 3-oxabutyl, 3,6-dioxaheptyl, 3,6,9-trioxadecyl, 3,6,9,12-tetraoxatridecyl, 3,6,9,12,15-pentaoxaheptadecyl, 3,6,9,12,15,18-hexaoxanonadecyl, 5-hydroxy-3-oxapentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 14-hydroxy-3,6,9,12-tetraoxatetradecyl, 3-thiabutyl, 5-hydroxy-3-azamethylpentyl, 5-hydroxy-3-azaethylpentyl, 3-azamethyl-6-oxaheptyl or 3-azamethylbutyl.

The preferred significance of R^7 is C_3-C_{12} alkyl which is interrupted by -O- and is unsubstituted or substituted by a hydroxyl group. 5-Hydroxy-3-oxapentyl or 3-oxabutyl is particularly preferred.

Preferred organic polymers or copolymers are those with a molecular weight from 1,000 to 150,000 and containing the structural unit of the formula I or that of the formula II, most preferably the structural unit of the formula I. Interesting polymers are also those which, as described above, contain the structural unit of the formula I, wherein R^1 is hydrogen, R^2 is hydrogen or carboxyl, R^3 is hydrogen and, if R^2 is hydrogen, is also methyl; n is 0, A is $-SR^6$, R^4 is cyclopropyl or ethyl, R^5 is tert-butyl or 1,2-dimethylpropyl, with the proviso that R^4 is only ethyl if R^5 is 1,2-dimethylpropyl, and R^4 is only cyclopropyl if R^5 is tert-butyl; and wherein R^6 is as defined above.

Preferred homopolymers are those containing the structural unit of the formula I or that of the formula II.

The most preferred polymers are those containing the structural unit of the formula I or that of the formula II, wherein R^1 , R^2 and R^3 are hydrogen and n is 0; or wherein R^1 , R^2 and R^3 are hydrogen and n is 1; or wherein R^1 and R^3 are hydrogen and R^2 is methyl; or wherein R^1 and R^3 are hydrogen and R^2 is $-COOH$.

Among these preferred polymers, particularly preferred polymers are in turn those in which R^1 , R^2 and R^3 are hydrogen and n is 0, or wherein R^1 and R^3 are hydrogen and R^2 is methyl.

Also preferred are polymers containing the structural unit of the formula I or that of the formula II, wherein R^4 is ethyl and R^5 is tert-butyl; or wherein R^4 is ethyl and R^5 is isopropyl; or wherein R^4 is ethyl and R^5 is 1,2-dimethylpropyl; or wherein R^4 is cyclopropyl and R^5 is isopropyl; or wherein R^4 is cyclopropyl and R^5 is tert-butyl. Among this group of compounds, those polymers are

particularly preferred wherein R^4 is cyclopropyl and R^5 is tert-butyl, or wherein R^4 is ethyl and R^5 is 1,2-dimethylpropyl.

Further preferred polymers are those having a molecular weight of 1,000 to 50,000 and containing the structural unit of the formula I, wherein n is 0 and R^1 is hydrogen, R^2 is hydrogen or carboxyl; or wherein n is 0 and R^3 is hydrogen or methyl; or wherein R^5 is tert-butyl, A is $-SR^6$ and R^6 is methyl; or wherein R^4 is cyclopropyl, A is $-SR^6$ and R^6 is methyl.

R^4 is preferably cyclopropyl, and R^5 is preferably isopropyl or tert-butyl.

The homopolymers defined above are good biocides for combating green and brown algae or diatoms. It is nevertheless often advantageous to modify these homopolymers by copolymerisation with at least one compound which contains one or more polymerisable double bonds.

The comonomers are preferably alk-1-enes of 2 to 6 carbon atoms, for example ethylene, propylene, but-1-ene, pent-1-ene or hex-1-ene, or vinyl halides, for example vinyl fluoride, vinyl chloride or vinyl bromide, or vinylidene halides, for example vinylidene chloride, or nitriles of α,β -unsaturated acids, for example acrylonitrile or methacrylonitrile, or α,β -unsaturated acids and the esters or halogen derivatives thereof, for example acrylic acid, methacrylic acid, crotonic acid, maleic acid, methacrylate, methyl methacrylate, ethyl methacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, isopropyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, glycidyl methacrylate, glycidyl acrylate or chloromethyl methacrylate; α,β -unsaturated carboxamides and derivatives thereof, for example acrylamide or methacrylamide, which derivative may contain sulfonic acid groups which, in turn, are in the form of sodium, potassium, copper or zinc salts; or are aromatic vinyl compounds, for example styrene, methyl styrene, vinyl toluene or α -chlorostyrene; or are vinyl ketones, for example methyl vinyl ketone, or vinyl

esters, for example vinyl acetate, said vinyl esters being used in particular for the preparation of polyalcohols; or are heterocyclic vinyl compounds, for example vinyl pyridine, vinyl pyrrolidone or N-vinylcarbazole; or they are vinyl ethers or unsaturated phosphonates; or dienes, for example butadiene, isoprene or chloroprene.

Particularly preferred comonomers are acrylic acid or methacrylic acid or derivatives of acrylic acid or of methacrylic acid. Also preferred are maleic acid and the derivatives thereof.

Most preferred are comonomers which are hydrophilic or which can be converted into hydrophilic groups. These monomers comprise for example vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylamide, vinyl methyl ether or vinyl (2-hydroxyethyl) ether. The preferred comonomer is vinyl acetate, which can be converted into polyvinyl alcohol by a subsequent hydrolysis step.

A further class of preferred comonomers is derived from ethylenically unsaturated organotin compounds of the formula III



wherein R^8 is hydrogen or carboxyl, R^9 is hydrogen or, if R^8 is hydrogen, is also methyl, and R^{10} is C_3 - C_6 alkyl or phenyl or substituted phenyl.

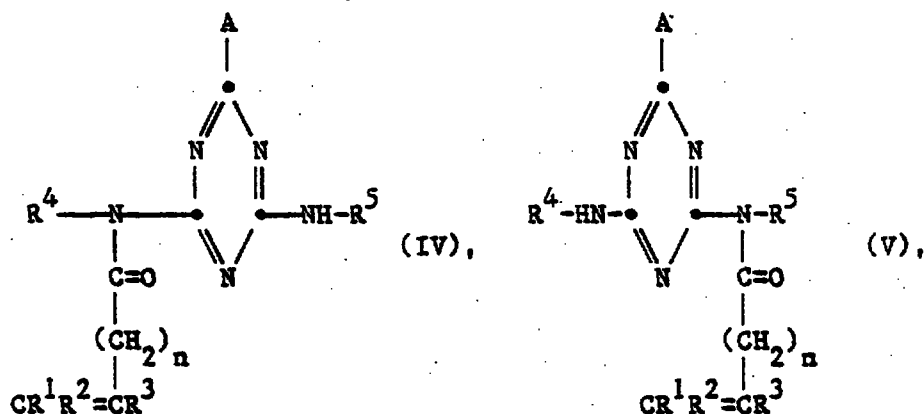
Further preferred comonomers are those derived from tri-organotin vinyl benzoates, in which the triorganotin radical is designated by $-SnR^{10}_3$.

R^{10} as C_3 - C_6 alkyl may be n-propyl, n-butyl, n-pentyl or n-hexyl. R^{10} as substituted phenyl may be tolyl or ethylphenyl, as well as p-chlorophenyl or p-bromophenyl. Most preferably R^{10} is n-butyl or phenyl.

As already mentioned, the copolymerisable component can be entirely absent or it may amount to 99.5 mol % of the polymer. Copolymers or terpolymers which contain up to 95 mol % of the comonomer are preferred.

The homopolymers or copolymers of this invention have a molecular weight of more than 1,000. However, the molecular weight can be up to 150,000, preferably up to 50,000. A molecular weight of 1,000 to 10,000 is preferred, with one of 1,000 to 5,000 being most preferred.

The monomers which are suitable starting materials for the polymerisation conform to the general formulae IV and V



wherein R^1 , R^2 , R^3 , R^4 , R^5 , A and n are as defined hereinbefore.

The starting materials of the formulae IV and V are novel and likewise constitute an object of the present invention.

In addition to their utility as starting materials for the biocidal polymers containing the structural unit of the formula I and/or that of the formula II, the monomers themselves are biocides.

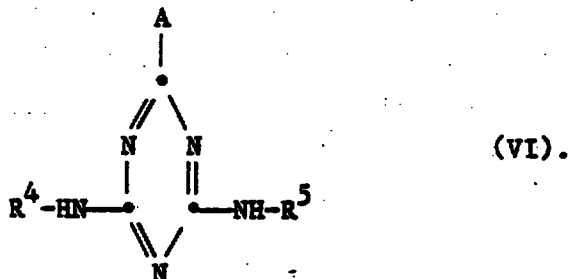
The preparation of the carboxamides of the formulae IV and V is effected in a manner known per se by reacting 2,6-diamino-4-alkylthio-s-triazines of the formula VI with acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, citraconic acid, dimethylmalonic acid, vinylacetic acid or reactive derivatives thereof, for example esters, chlorides or anhydrides, preferably with the carboxylic acid chlorides.

The reaction is preferably carried out in an inert organic solvent. It is preferred to use 1 mole of α,β -unsaturated carboxylic acid or derivative thereof per mole of compound of the formula VI.

If an acid halide is used, the process is carried out in the presence of a base, for example of a tertiary amine such as triethylamine, diisopropylethylamine, N,N-diethylaniline or pyridine. or in the presence of an anhydrous alkali metal carbonate or alkaline earth metal carbonate, or of an alkali metal bicarbonate such as MgCO_3 , NaHCO_3 , Na_2CO_3 or K_2CO_3 , or of an alkali metal hydride or alkaline earth metal anhydride. If an acid anhydride is used instead of the acid chloride, then the base may be dispensed with. It is particularly preferred to use sodium hydride.

The organic solvents used in the above described process variants must be inert to the reactants. Examples of suitable solvents are aliphatic hydrocarbons such as hexane or ligroin, aromatic hydrocarbons such as benzene, toluene or xylene; chlorinated hydrocarbons such as methylene chloride or chloroform; amides such as hexamethylenephosphoric triamide; or ethers such as dioxan, 1,2-dimethoxyethane, diethyl ether or tetrahydrofuran, and, in particular, dimethylformamide. It is also possible to use halide free solvents for the subsequent polymerisation of the monomers of the formula IV or V. It is not absolutely necessary to isolate the intermediates of the formula IV or V and further reaction to give the polymers or copolymers of the invention can be carried out immediately in a single step.

The s-triazines of the formula VI, wherein R^4 , R^5 and A are as defined above, are known compounds



The compounds can be prepared by a process analogous to that described in US patent specification 3,799,925 by reacting a 2,4-dichloro-6-alkylamino-s-triazine with a primary aliphatic amine to give a 2-alkylamino-4-chloro-alkylamino-s-triazine and, if desired, converting this compound with an alkyl mercaptan or an alkyl alcoholate into the corresponding 4-alkylthio or 4-alkoxy derivative respectively.

The triazines of formula VI are known algicides. In particular, derivatives in which $A = -SCH_3$, $R^4 = \text{ethyl}$ and $R^5 = 1,2\text{-dimethylpropyl}$, or $A = -SCH_3$, $R^4 = \text{cyclopropyl}$ and $R^5 = \text{tert-butyl}$, are described as sea water algicides in EP 3749.

The polymers of this invention can be prepared in two different ways. On the one hand it is possible to polymerise the functionalised monomers of the formulae IV and/or V, or to react a polycarboxylic acid, or a reactive derivative thereof, for example a polycarboxylic acid chloride, preferably polyacryloyl chloride, or a polycarboxylic anhydride, preferably copolymers or terpolymers of maleic anhydride, with the appropriate diamino-s-triazine of the formula VI in a manner known per se.

The preparation of suitable polyacryloyl chlorides is described for example in *Chimia* 19, 235 (1959). The monomers of the formula IV or V can be polymerised by known methods which are described e.g. in Houben-Weyl 14 (1), 1010 (1962).

Suitable reactions are in particular those known as radical and anionic homo- and copolymerisation. The polymerisation is controlled in known manner by initiators and regulators or chain-terminators. In this manner it is possible to obtain polymers of the desired molecular weight. The polymerisation can be carried out in substance, in solution, in dispersion, in emulsion, in suspension, or as a so-called bead polymerisation.

Suitable initiators for the radical homo- or copolymerisation are for example azo compounds and also reducing agents. However, azo compounds are especially preferred. Particularly suitable azo compounds are those in which the azo group is linked on both sides to tertiary C-atoms which, in addition to alkyl groups, also carry nitrilo or ester groups. Thus, for example, α, α' -azoisobutyronitrile is an important representative of this class of initiators. If the polymerisation is initiated by a reducing agent, then suitable initiators are either metal ions of lower valency or metal-free compounds which can be readily oxidised, for example Ag^+ , Fe^+ , Ti^{3+} , hydrogen sulfite, sulfite, thiosulfate, mercaptans, sulfines, amines, endiols (sugars), benzoin/ Fe^{2+} or hydrogen sulfite/ Fe^{2+} . Whereas in the case of the azo compounds the nature of the initiator solely influences the rate of polymerisation, the average degree of polymerisation, the nature of the end groups or the number of branchings, but not the polymerisability, not every reducing agent is suitable for every unsaturated compound. The molecular weight of the polymer is best controlled with suitable regulators. Examples are mercaptans such as n-butyl mercaptan or dodecyl mercaptan, and other organic sulfur compounds such as diisopropylxanthogen disulfide, as well as aliphatic aldehydes and acetals, or allyl compounds such as allyl alcohol. The reaction temperatures are known to the skilled person and for radical polymerisation are in the range from -20° to $+200^\circ\text{C}$, preferably from $+20^\circ$ to $+150^\circ\text{C}$, depending on the components employed.

Suitable initiators for anionic polymerisation are organometallic compounds such as diethyl zinc or diisobutyl zinc, naphthalene sodium, n-amyl sodium, cyclopentadienyl sodium, n-butyl lithium or triethyl aluminium. Suitable initiators are also bases such as hydroxides of alkali metals or alkaline earth metals, alcoholates, amides and hydrides. Particularly preferred initiators are hydrides of alkali metals or alkaline earth metals, preferably NaH. Instead of the regulators employed in radical polymerisation, compounds which react with the growing chain end are used for anionic polymerisation. These compounds comprise e.g. water, alcohols, acids and amines. The temperature for this reaction variant is in the range from -100° to $+200^{\circ}\text{C}$, preferably from -20° to $+150^{\circ}\text{C}$, and is known to the skilled person for each desired type of polymer.

It is also possible to use heat, light or high-energy irradiation for the polymerisation, in which case the reaction proceeds in accordance with the radical mechanism. Examples of suitable catalysts for photoinitiated polymerisation are benzoin ethers, benzil ketals, α -dialkoxyacetophenone derivatives or aromatic ketone-amine combinations.

The methods described are suitable in principle for both homopolymerisation and for copolymerisation reactions. Statistical copolymers or also block copolymers are obtained in this manner, depending on the choice of the copolymerisation parameters.

The present invention also relates to a process for the preparation of a polymer which contains the structural unit of the formula I and/or of the formula II, which process comprises polymerising monomers of the formula IV and/or V, alone or together with further ethylenically unsaturated monomers. —

The invention further relates to an organic polymer obtainable by homopolymerisation and copolymerisation of a functionalised monomer of the formula IV/ and/or V.

The invention additionally relates to a process for the preparation of a polymer which contains the structural unit of the formula I, which comprises reacting polyacryloyl chloride, polymethacryloyl chloride, polymaleic anhydride or copolymers or terpolymers of maleic anhydride with one or two 2,6-diamino-s-triazines of the formula VI, but preferably with 2-cyclopropylamino-4-methylthio-6-tert-butylamino-s-triazine.

Finally, the invention also relates to an organic polymer obtainable by reacting an s-triazine of the formula VI and a polyacryloyl chloride, a polymethacryloyl chloride, a polymaleic anhydride or a copolymer or terpolymer of maleic anhydride.

The compounds of the present invention are used wherever objects which it is desired to protect against the growth of algae or of diatoms are exposed to water, especially to sea water. Such objects are in particular ship's hulls, hydraulic structures, buoys or fishing nets. The protective action of the compounds of this invention also extends to cooling and pipe systems through which water flows, and also to structures which come in contact with water, to swimming baths or reservoirs. Quite generally, the functionalised polymers protect all materials which come in contact with water from growth of algae, e.g. wood, cellulose, textiles and leather, paints, lacquers, e.g. antifouling paints, disperse paints, disperse coatings and similar coating materials, optical and other glasses, plastics materials, rubber and adhesives, as well as other materials.

Depending on the end use, the compounds are employed in the concentration ranges known to the skilled person. The limits of the useful concentrations are indicated by the following values: whereas concentrations in the ppm range suffice in cooling water, concentrations of up to 60 % by weight are usual in antifouling paints.

The compounds can be used in pure form. They can also be dissolved or suspended in liquid media, in which case wetting agents or emulsifiers can promote the homogeneous distribution of the active ingredient to form homogeneous dispersions. Preferably further biocides can be added. For cooling water applications, the polymer can also be applied in tablet form, if appropriate also in combination with other water treatment agents.

A particularly preferred field of use is that of protective coating compositions, especially antifouling paints as well as disperse paints or disperse coatings which, in addition to the conventional basic materials and additives, contain 0.5 to 60 % by weight, preferably 3 to 25 % by weight, based on the total composition, of a polymer of this invention or a mixture of such polymers. The polymers of this invention or mixtures thereof are also suitable for the preparation of self-polishing antifouling coatings.

Conventional basic materials for antifouling paints are the raw materials for paints and varnishes which are known to the skilled person and designated as binders, such as natural and synthetic resins, homopolymers and copolymers with vinyl chloride, vinylidene chloride, styrene, vinyl toluene, vinyl esters, acrylic acid and methacrylic acid and the esters thereof; also chlorinated rubber, natural and synthetic rubber which may be chlorinated or cyclised, as well as reactive resins such as epoxy resins, polyurethane or unsaturated polyesters, which, if desired, can be converted into film-forming high molecular products by adding hardeners. The polymers of this invention can also be used as binders.

The conventional binders can be liquid or in the form of solutions. If dissolved binders and also thermoplasts are used, a protective film can also be formed by evaporating the solvent. Solid coating compounds can be applied to solid objects, for example by powder coating methods. Further customary basic materials are for example tar, modifiers, dyes, inorganic or organic pigments, fillers and hardeners.

Finally, the compounds of this invention can also be used in elastomeric coatings or also in plastics materials.

A further field of application for the polymers of the invention comprises their use in disperse paints, in disperse coatings and in cooling water. For this last mentioned utility they are preferably used in combination with incrustation and/or corrosion inhibitors, for example in combination with polyacrylic acid, polymethacrylic acid, hydrolysed polymaleic anhydride or hydrolysed copolymers of maleic anhydride and olefinic monomers. It is also possible to use combinations with polyphosphates.

In practice, algicides are often used together with other biocides. In antifouling paints, the combination with a biocide which acts against animal growth organisms is advantageous. Examples of such biocides are metallic copper, for example in powder form, as well as Cu_2O , zinc oxide, triorganotin compounds such as tributyltin oxide, tributyltin fluoride or triphenyltin chloride; or quite generally those compounds which are known to the skilled person as effective against animal growth. In particular, it is also possible to charge the homopolymers or copolymers of the invention, which contain free carboxyl groups, with metal ions by salt formation, preferably using Cu^+ , Cu^{2+} or Zn^{2+} ions. The combination of a fungicide is expedient in disperse paints and disperse coatings. In water treatment it is preferred to use a combination with a bactericide in order to combat myxobacteria, whereas the polymer of the invention acts in particular against slime-forming algae. A combination with further algicides is also often advantageous.

Accordingly, the invention also relates to an algicidal composition containing a functionalised polymer having a structural unit of the formula I and/or of the formula II, and optionally containing further biocides.

Such a composition is preferably a protective coating composition, in particular an antifouling paint, a disperse paint, a disperse coating or a disperse lacquer.

The polymers, or mixtures of polymers, of this invention are particularly effective agents against algae or diatoms which live in fresh water or sea water, especially against species of algae which occur in sea water. The most important and most frequently encountered species which may be mentioned here are *Enteromorpha* and *Amphora*.

The following examples are presented for the purpose of illustration only and are not to be construed to limit the nature or scope of the instant invention in any manner whatsoever.

Preparatory Examples

1. Preparation of polyacrylic acid fixed 2-cyclopropylamino-4-methylthio-6-tert-butylamino-s-triazine by reacting the triazine with acryloyl chloride.

A suspension of 37.9 g (1.58 moles) of NaH (purified in hexane) in 400 ml of dimethylformamide is added dropwise, under N_2 , to an ice-cooled solution of 400 g (1.58 moles) of the triazine derivative in 1800 ml of dimethylformamide. The reaction mixture is stirred for 30 minutes at 0°C and then for 2 hours at room temperature. The solution is again cooled to 0°C and 144.5 g (1.58 moles) of freshly distilled acryloyl chloride in 130 ml of dimethylformamide are slowly added dropwise. The reaction mixture is stirred for 30 minutes at 0°C and then for 2 hours at 50°C, and concentrated by evaporation at 70°C (bath temperature) in vacuo. The residue (approx. 40 to 50 % solution) is poured into water. The precipitate is rapidly isolated by filtration, washed with water, dried, and dissolved in ethyl acetate. The organic solution is dried over

Na_2SO_4 , filtered, and concentrated in vacuo to about 800 ml at $60^\circ\text{--}70^\circ\text{C}$ (bath temperature). After precipitation of this concentrated solution with hexane, the polymer so obtained is stirred in hexane/ethyl acetate (95:5) and then in hexane, isolated by filtration and dried.

Yield: 331 g (68.1 % of theory); $\bar{M}_n$: 2450 (determined by vapour pressure osmometry).

2. Preparation of polyacrylic acid fixed 2-cyclopropylamino-4-methylthio-6-tert-butylamino-s-triazine by reacting the triazine with polyacryloyl chloride.

A suspension of 1.2 g (0.05 mole) of NaH (purified in hexane) in 40 ml of dimethylformamide is added dropwise, under N_2 , to an ice-cooled solution of 12.65 g (0.05 mole) of the triazine derivative in 100 ml of dimethylformamide. The reaction mixture is stirred for 1/2 hour at 0°C and then for 2 hours at room temperature. The solution is again cooled to 0°C and 4.53 g (0.05 mole) of polyacryloyl chloride (50 % in dioxan) are slowly added dropwise. The solution is stirred for 30 minutes at 0°C and then for 16 hours at room temperature. The mixture is precipitated with water. The precipitated solid is dried, dissolved in 50 ml of CH_2Cl_2 and precipitated with methanol. After filtration and drying there is obtained a fraction A: 3.33 g (21 %) with $\bar{M}_n \sim 7700$. The filtrate is concentrated to half its volume and the residue is precipitated in pentane. A second fraction (fraction B) is obtained: 2.9 g (18 %) with $\bar{M}_n = 2250$ (determined by vapour pressure osmometry).

3. Preparation of 2-cyclopropylamino-4-methylthio-6-(N-tert-butylmethacrylamido)-s-triazine.

In a three-necked flask equipped with condenser, stirrer, thermometer and dropping funnel, a solution of 25.35 g (0.1 mole) of 2-cyclopropylamino-4-methylthio-6-(N-tert-butylamino)-s-triazine in 250 ml of dry dichloromethane is cooled in an ice bath to $0^\circ\text{--}5^\circ\text{C}$, with exclusion of moisture, and 10.5 g (0.01 mole) of triethylamine

are added. With efficient stirring, a solution of 10.46 g (0.1 mole) of methacryloyl chloride (distilled and stabilised with 0.01 % by weight of 2,6-di-tert-butyl p-cresol) in 40 ml of dry dichloromethane is added dropwise at 0°-3°C over 60 minutes. The mixture is stirred for a further 5 hours in the ice bath and then stirred for 10 hours at room temperature. The resultant suspension of triethylamine hydrochloride is filtered, the filtrate is concentrated in a rotary evaporator and the solution of the residue is filtered through silica gel with diethyl ether as eluant. The diethyl ether is removed by evaporation and the residue is recrystallised from hexane/diethyl ether to give a crystalline product with a melting point of 115°-117°C. Yield: 20.5 g (64 % of theory). The structure of the product is confirmed by IR, ¹H and ¹³C-NMR spectroscopy.

4. Preparation of 2-cyclopropylamino-4-methylthio-6-(N-tert-butylacrylamido)-s-triazine.

Following the procedure described in Example 3, 2-cyclopropylamino-4-methylthio-6-(N-tert-butylamino)-s-triazine in dichloromethane is reacted with triethylamine and acryloyl chloride. The product obtained melts at 119°-121°C and the indicated structure is confirmed by IR, ¹H or ¹³C-NMR spectroscopy.

5. Polymerisation of 2-cyclopropylamino-4-methylthio-6-(N-tert-butyl-methacrylamido)-s-triazine.

In a three-necked flask equipped with condenser, stirrer, thermometer and gas inlet pipe, 11.2 g of 2-cyclopropylamino-4-methylthio-6-(N-tert-butyl-methacrylamido)-s-triazine (prepared according to Example 3) are dissolved in 200 ml of absolute dry distilled tetrahydrofuran. This solution is scavenged with dry nitrogen to expel atmospheric oxygen and cooled to 0°-3°C. At this temperature 1.5 ml of a 1.6 molar solution of n-butyllithium in hexane are added and the orange solution is stirred for 3 hours at 0°-3°C and for

12 hours at 25°C. After addition of a further 0.5 ml of n-butyl-lithium solution, the reaction mixture is heated for 1 hour to 65°C, cooled, and filtered. The dissolved polymer is isolated by precipitation in a 9:1 mixture of hexane/diethyl ether. After further recrystallisation from ethyl acetate/hexane/diethyl ether, the polymer is free from monomers and oligomers and has a molecular weight of $\bar{M}_n$ 3000 (determined by vapour pressure osmometry; concentration 0.72 % in CHCl_3).

The yield is 7.9 g, corresponding to 70.5 % of theory.

Use Examples

An antifouling paint composition is prepared, in which a mixture of polymers of the invention is used as binder (without using conventional binders) in accordance with the following recipe A:

polyacrylic acid fixed

2-cyclopropylamino-4-methylthio-6-tert-butyl-amino-s-triazine with an average mol. wt. of 4000 (obtained according to Example 1)

3.80 g

polyacrylic acid fixed 2-cyclopropyl-amino-4-methylthio-6-tert-butylamino-s-triazine with an average mol. wt. of 2000 (obtained according to Example 2)

5.20 g

(the triazine content in these polymers is about 65 %)

phosphate plasticiser (REOFOS® 65)

0.45 g

epoxidised soybean oil (IRGAROL® SA 39)

0.43 g

talcum

3.36 g

iron oxide red

5.76 g

barytes

5.28 g

tributyltin fluoride

4.20 g

solvent with a high content of aromatics (Shell Sol A)

22.50 g

xylene

11.20 g

methyl isobutyl ketone

22.50 g

This antifouling paint composition A is applied to sand-blasted 10 x 15 cm metal plates which are coated with primer and provided with a coat of red lead paint based on a vinyl chloride copolymer. A technically perfect finish is obtained with this composition. After storage for about 4 weeks, the coated metal plates, in a wooden frame, are submerged vertically to a depth of about 30 cm from a raft in the Mediterranean Sea and assessed for the growth of algae in accordance with the following rating:

10 = completely free from growth

0 = totally overgrown

intermediate ratings indicate the extent of growth.

The following results with respect to the growth of algae are observed after 8, 12 and 16 months:

Antifouling paint composition	A
evaluation after 8 months	10
evaluation after 12 months	10
evaluation after 16 months	10

After 8, 12 or 16 months, coating A exhibits no blemishes of any kind such as blistering, flaking, colour loss or the like.

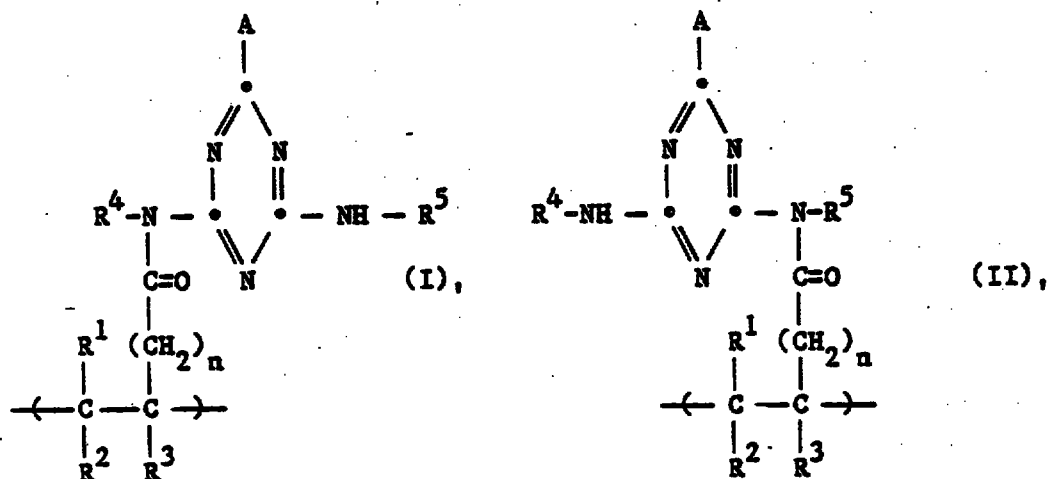
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CLAIMS

1. An organic polymer having a molecular weight from 1,000 to 150,000 and containing the structural unit of the formula I and/or of the formula II



wherein R^1 is hydrogen, R^2 is hydrogen or $-\text{COOR}^7$ and R^3 is hydrogen or methyl, and R^1 additionally is methyl if R^2 is $-\text{COOR}^7$ and if R^3 is methyl, and wherein R^2 additionally is methyl if R^1 and R^3 are hydrogen; n is 0 or, if R^1 , R^2 and R^3 are hydrogen, is 1; R^4 is straight chain C_2 - C_6 alkyl or C_3 - C_6 cycloalkyl; R^5 is branched C_3 - C_6 alkyl; A is $-\text{SR}^6$, $-\text{OR}^6$ or $-\text{Cl}$, in which R^6 is C_1 - C_3 alkyl; R^7 is hydrogen, C_1 - C_{20} alkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, phenyl, C_5 - C_{12} cycloalkyl, C_7 - C_{14} aralkyl, C_7 - C_{14} alkaryl, C_2 - C_{20} alkyl which is substituted by one or two hydroxyl groups or is C_3 - C_{20} alkyl which is interrupted by 1 to 5 identical or different members selected from $-\text{O}-$, $-\text{S}-$ and $-\text{N}(\text{CH}_3)-$, and is unsubstituted or substituted by a hydroxyl group, with the proviso that any recurring hetero atoms must be separated by at least one methylene group; or a copolymer thereof with at least one compound which contains a polymerisable double bond, such that the molar ratio of the component or components of the formula I and/or of the formula II to the co-monomer component may be up to 0.5:99.5.



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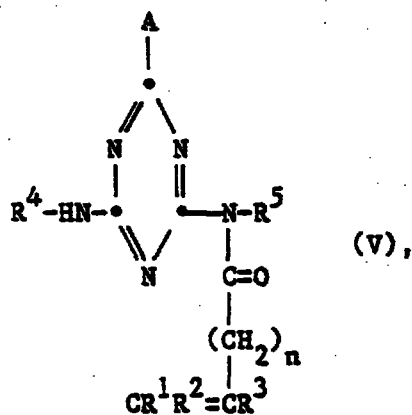
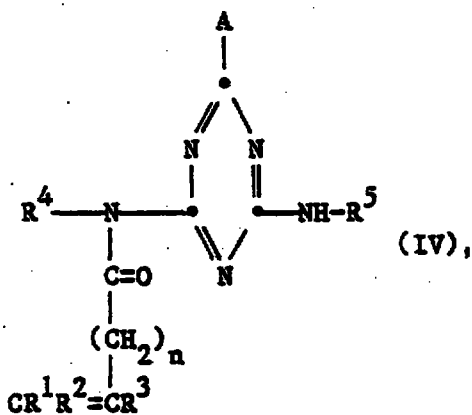
2. An organic homopolymer containing the structural unit of the formula I according to claim 1.
3. An organic homopolymer containing the structural unit of the formula II according to claim 1.
4. An organic copolymer or terpolymer containing the structural unit of the formula I according to claim 1.
5. An organic copolymer or terpolymer containing the structural unit of the formula II according to claim 1.
6. An organic polymer or copolymer with a molecular weight of 1,000 to 50,000 according to claim 1, containing the structural unit of the formula I, wherein R^1 is hydrogen, R^2 is hydrogen or carboxyl, R^3 is hydrogen and, if R^2 is hydrogen, is also methyl; n is 0, A is $-SR^6$, R^4 is cyclopropyl or ethyl, R^5 is tert-butyl or 1,2-dimethylpropyl, with the proviso that R^4 is only ethyl if R^5 is 1,2-dimethylpropyl, and R^4 is only cyclopropyl if R^5 is tert-butyl; and wherein R^6 is C_1-C_3 alkyl.
7. An organic copolymer according to claim 4, containing as comonomers acrylic acid or a derivative thereof or methacrylic acid or a derivative thereof.
8. An organic copolymer according to claim 4, containing maleic acid or a derivative thereof as comonomer.
9. An organic polymer according to claim 1, wherein R^1 , R^2 and R^3 are hydrogen and n is 0.
10. An organic polymer according to claim 1, wherein R^1 and R^3 are hydrogen and R^2 is carboxyl.
11. An organic polymer according to claim 1, wherein n is 0 and R^3 is hydrogen.

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12. An organic polymer according to claim 1, wherein R_3 is methyl.
13. An organic polymer according to claim 1, wherein A is $-SCH_3$.
14. An organic polymer according to claim 1, wherein R^5 is tert-butyl and A is $-SCH_3$.
15. An organic polymer according to claim 1, wherein R^4 is cyclopropyl and A is $-SCH_3$.
16. An organic polymer according to claim 1, which contains the structural unit of the formula I and/or that of the formula II in an amount from 5 to 100 mol %.
17. An ethylenically unsaturated monomer of the formula IV or V



wherein R^1 , R^2 , R^3 , R^4 , R^5 , A and n are as defined in claim 1.

18. A composition of matter containing at least one polymer containing the structural unit of the formula I and/or that of the formula II according to claim 1.



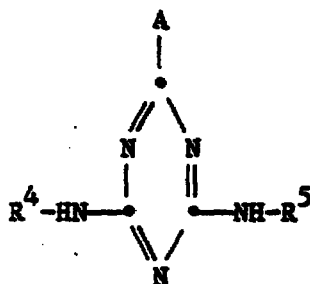
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19. A process for the preparation of a polymer, which comprises polymerising the monomer of the formula IV and/or V according to claim 17.

20. A process for the preparation of a polymer according to claim 19, which comprises polymerising the monomer of the formula IV and/or V together with further ethylenically unsaturated monomers.

21. A process for the preparation of a functionalised polymer according to claim 1, which comprises reacting a triazine of the formula VI



(VI).

wherein R^4 , R^5 and A are as defined in claim 1, with polyacryloyl chloride, polymethacryloyl chloride, polymaleic anhydride or with a copolymer or terpolymer of maleic anhydride.

22. Use of a polymer according to claim 6 as algicide in anti-fouling paints.

23. Use of a polymer according to claim 1 as algicide in disperse paints or disperse coatings.

24. Use of a polymer according to claim 1 as algicide in circulating cooling systems.

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25. An organic polymer as claimed in claim 1, substantially as hereinbefore described with reference to any one of Examples 1, 2 and 5.

26. A compound as claimed in claim 17 substantially as hereinbefore described with reference to Example 3 or 4.

27. A composition as claimed in claim 18 substantially as hereinbefore described with reference to the foregoing use Example.
