DESCRIPTION

MAIN-CHAIN DEGRADABLE COPPER POLYACRYLATE RESIN, PREPARATION METHOD THEREFOR AND APPLICATION THEREOF

FIELD OF THE INVENTION

The present invention belongs to the technical field of marine antifouling materials, and relates to a copper polyacrylate resin for marine antifouling coatings, in particular to a main-chain degradable copper polyacrylate resin, a preparation method therefor and an application thereof; the resin is used to prepare marine antifouling coatings.

BACKGROUND OF THE INVENTION

In recent years, with limited land resources having been over-exploited, people have gradually turned their eyes and footprints to the oceans, and thus a sea fever has been set off. However, the serious sea creature fouling problem lies in front of people and has been plaguing researchers all over the world. At present, self-polishing marine antifouling coatings are the means with the highest commercial level, the most mature technology and the longest service life. Resins for mainstream self-polishing antifouling coatings include silane polyacrylate resin, zinc polyacrylate resin and copper polyacrylate resin. Among them, the copper ester bond, more unstable than the silicon ester bond and the zinc ester bond, has a higher hydrolysis rate under seawater attack. In addition, copper ions produced by hydrolysis of the copper ester bond have antifouling and bactericidal effects.

However, the existing self-polishing technology is mainly based on the side-chain hydrolysis, with its performance having certain requirements for the navigational duration and speed. In a static state, it is difficult to achieve the desired self-polishing effect by the flushing of seawater alone, so the static antifouling effect is not good. Moreover, after the side chain is hydrolyzed, the macromolecular main chain leaves the coating surface and enters the seawater. Because the macromolecular main chain cannot be degraded, it will cause microplastic pollution to the ocean, which in the long run will seriously threaten the stability and safety of the marine ecosystem. By introducing a degradable polyester

structure into the main chain of the copper polyacrylate resin, it is expected to produce an efficient and long-life antifouling coating resin.

CONTENTS OF THE INVENTION

In view of the deficiencies of the resin materials and technologies for the marine antifouling coatings, an object of the present invention is to provide a main-chain degradable copper polyacrylate resin having a polyester structure in the main chain and a copper ester bond in the side chain. The main-chain degradable copper polyacrylate resin can not only meet the static marine antifouling demand, but also solve the problem of marine microplastic pollution.

Another object of the present invention is to provide a preparation method for the above-mentioned main-chain degradable copper polyacrylate resin.

Still another object of the present invention is to provide an application of the above-mentioned main-chain degradable copper polyacrylate resin. The main-chain degradable copper polyacrylate resin is used for preparing marine antifouling coatings.

The objects of the present invention are achieved through the following technical solution:

A main-chain degradable copper polyacrylate resin is prepared from the following components in parts by weight:

Acrylate prepolymer	100
Copper-containing compound	5-50
Monocarboxylic acid	0-75
Organic solvents	5-150

The 100 parts by weight of the acrylate prepolymer are based on the total amount of reactive monomers (cyclic monomers, vinyl monomers, (methyl)propenoic acid) in the acrylate prepolymer.

The copper-containing compound is one or more of copper oxide, copper hydroxide, copper chloride, copper acetate, and copper propionate.

The monocarboxylic acid is one or more of propenoic acid, methylpropenoic acid, formic acid, acetic acid, propionic acid, benzoic acid, octanoic acid, isooctanoic acid,

stearic acid, isostearic acid, naphthenic acid, itaconic acid, maleic acid, oleic acid, palmitic acid, and rosin acid.

The acrylate prepolymer is mainly prepared from the following components:

50-100 parts by weight of a solvent, 5-95 parts by weight of a cyclic monomer, 0-95 parts by weight of a vinyl monomer, 5-30 parts by weight of (methyl)propenoic acid, and 0.01-10 parts by weight of an initiator; the (methyl)propenoic acid means methylpropenoic acid or propenoic acid.

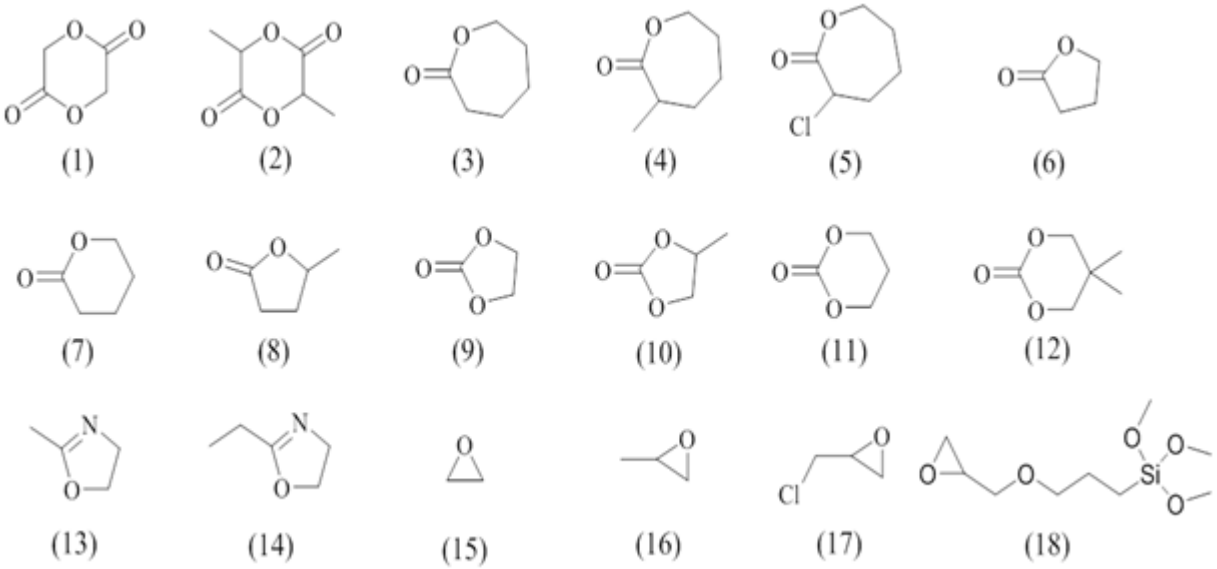
The solvent is one or more of a hydrocarbon solvent, an alcohol solvent, a ketone solvent, and an ester solvent.

The hydrocarbon solvent is one or more of toluene and xylene; the alcohol solvent is one or more of isopropanol, n-butanol, isobutanol, and propylene glycol methyl ether; the ketone solvent is one or more of methyl ethyl ketone, methyl isobutyl ketone, acetone, butanone, and cyclohexanone; the ester solvent is one or more of ethyl acetate and butyl acetate.

The cyclic monomer is one or more of the following 38 compounds: (1) glycolide, (2) lactide, (3) ε-caprolactone, (4) 2-methyl-ε-caprolactone, (5) 2-chloro-ε-caprolactone, (6) γ-butyrolactone, (7) δ-valerolactone, (8) γ-valerolactone, (9) vinyl carbonate, (10) propylene carbonate, (11) trimethylene cyclocarbonate, (12) 2,2-dimethyltrimethylene cyclocarbonate, (13) 2-methyl-2-oxazoline, (14) 2-ethyl-2-oxazoline, (15) ethylene oxide, (16) propylene oxide, (17) epichlorohydrin, (18) γ-glycidyl ether oxypropyl trimethoxysilane, (19) 2-methylene-1,3-dioxocyclopentane, (20) 2-methylene-1,3-dioxocyclopentane, (21) 2-methylene-4-alkyl-1,3-dioxocyclopentane, (22) 2,4-dimethylene-1,3-dioxocyclopentane, (23) 2-methylene-1,3-dioxo-4,5-benzocyclopentane, (24) 2-methylene-1,3-dioxocyclohexane, (25) 2,5-dimethylene-1,3-dioxocyclohexane, (26) 2-methylene-5-phenyl-1,3-dioxocyclohexane, (27) 2-methylene-4-alkyl-1,3-dioxocyclohexane, (28) 2-methylene-1,3-dioxocycloheptane, (29) 2-methylene-5-alkyl-1,3-dioxocycloheptane, (30) 2-methylene-4,7-dimethyl-1,3-dioxocycloheptane, (31) 2-methylene-1,3-dioxo-5,6-benzocycloheptane, (32)

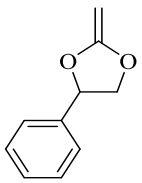
2-methylene-5-phenyl-1,3-dioxocycloheptane, (33) 2-ethylidene-1,3-dioxocycloheptane, (34) 2-methylene-1,3-dioxo-5-cycloheptene, (35) 2-ethylidene-4-alkyl-1,3-dioxocyclopentane, (36) 2-ethylidene-1,3-dioxocyclohexane, (37) 2-allylidene-4-phenyl-1,3-dioxocyclopentane, and (38) 2-ethylidene-1,3-dioxo-5,6-benzocycloheptane.

The cyclic-monomer structural formulae of the compounds 1 to 38 are as follows:

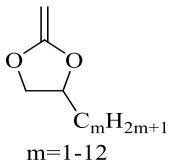




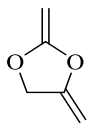
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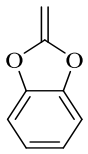
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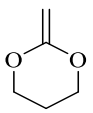
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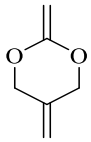
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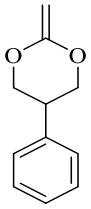
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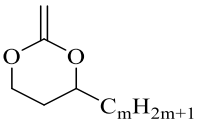
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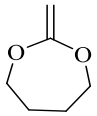
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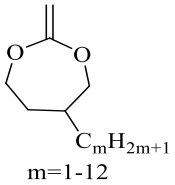
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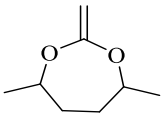
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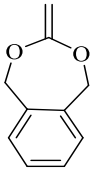
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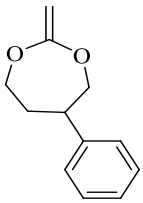
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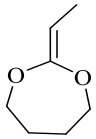
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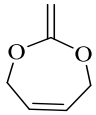
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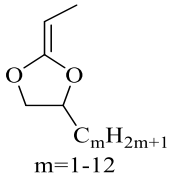
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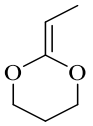
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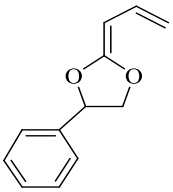
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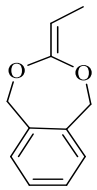
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Wherein m = 1-12 indicates that m is an integer of 1 to 12.

The vinyl monomer is one or more of acrylates, methylacrylates, hydroxyl-terminated acrylates, hydroxyl-terminated methylacrylates, cyclic hydrocarbon acrylates, cyclic hydrocarbon methylacrylates, polyolefin glycol acrylates, and polyolefin glycol methylacrylates.

The acrylates are one or more of methyl acrylate, ethyl acrylate, 2-methoxyethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, octyl acrylate, isooctyl acrylate, dodecyl acrylate, and stearic acrylate.

The methylacrylates are one or more of methyl methylacrylate, ethyl methylacrylate, 2-methoxyethyl methylacrylate, propyl methylacrylate, isopropyl methylacrylate, n-butyl methylacrylate, isobutyl methylacrylate, tert-butyl methylacrylate, octyl methylacrylate, isooctyl methylacrylate, dodecyl methylacrylate, and stearic methylacrylate.

The hydroxyl-terminated acrylates are one or more of hydroxyethyl acrylate and hydroxypropyl acrylate.

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The cyclic hydrocarbon acrylates are one or more of phenyl acrylate, cyclohexyl acrylate, 4-methylcyclohexyl acrylate, and 4-tert-butylcyclohexyl acrylate.

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The polyolefin glycol acrylates are polyethylene glycol acrylate; and the degree of polymerization of the polyethylene glycol is preferably from 1 to 10.

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The initiator is one or more of phosphazene, phosphazene salt, oxidized phosphazene, azobisisobutyronitrile, azobisisovaleronitrile, benzoyl peroxide, di-tert-butyl peroxide, and tert-butyl peroxy-2-ethylhexanoate.

When the acrylate prepolymer is prepared, the components further comprise a low molecular alcohol or a low molecular amine or a telogen, with the low molecular alcohol or low molecular amine or telogen compounded with an initiator.

The low molecular alcohol is one or more of aliphatic or aromatic alcohols having 1 to 12 carbon atoms.

The low molecular amine is one or more of aliphatic or aromatic amines having 1 to 12 carbon atoms.

The total amount of the initiator and the low molecular alcohol or low molecular amine is 0.01-10 parts by weight.

The telogen is one or more of n-dodecyl mercaptan, tert-dodecyl mercaptan, isooctyl 3-mercaptopropionate, ethyl hexanol 3-mercaptopropionate, pentaerythritol tetra(3-mercaptopropionate), and α-methylstyrene dimer. Preferably, the telogen is one or more of α-methylstyrene dimer and n-dodecyl mercaptan.

The amount of telogen used is 0.5 to 5 parts by weight, and the weight ratio of the telogen to the initiator is (0.5 to 5):(0.01 to 10).

The organic solvent is a hydrocarbon solvent, preferably one or more of toluene and xylene.

The preparation method for the main-chain degradable copper polyacrylate resin comprises the following steps:

(1) Synthesis of the acrylate prepolymer:

In an inert gas, with 50-100 parts by weight of a solvent used as a reaction medium, under the action of 0.01-10 parts by weight of an initiator, 5-95 parts by weight of a cyclic monomer, 0-95 parts by weight of a vinyl monomer, and 5-30 parts by weight of (methyl)propenoic acid are reacted at 70℃ to 120℃ for 5-18 h to obtain an acrylate prepolymer;

(2) synthesis of the copper polyacrylate resin:

with 5-150 parts by weight of an organic solvent used as a reaction medium, 100 parts by weight of the acrylate prepolymer, 5-50 parts by weight of a copper-containing compound, and 0-75 parts by weight of a monocarboxylic acid are reacted at 70℃ to 180℃ for 4-10 h to obtain copper polyacrylate resin.

The main-chain degradable copper polyacrylate resin has a copper content of 1% to 20%, preferably 5% to 10%.

The number average molecular weight Mn (measured by GPC using polystyrene as a guide sample) of the main-chain degradable copper polyacrylate resin is 3,000-50,000, preferably 3,000-30,000.

The main-chain degradable copper polyacrylate resin has an acid value of 50-350 mgKOH/g, preferably 70-250 mgKOH/g.

The main-chain degradable copper polyacrylate resin is used for preparing marine antifouling coatings.

The main-chain degradable copper polyacrylate resin provided by the present invention is a random copolymer composed of a polyester chain segment, a vinyl monomer and a vinyl copper ester unit, and prepared by a post-grafting method. The

present invention introduces a degradable polyester chain segment into the main chain of the copper polyacrylate resin, so that in the materials involved not only the copper ester bonds at the side chain can be hydrolyzed but also the polyester structure at the main chain can be degraded under seawater attack. By adjusting the content of copper and cyclic monomers, the purpose of synergistic hydrolysis and degradation rates is achieved, and the application requirements of static antifouling are met. Besides, with the continuous progress of hydrolysis and degradation, the materials can eventually degrade into small molecules, solving the problem of marine microplastic pollution.

Compared with the prior art, the present invention has the following advantages and outstanding effects:

(1) The present invention introduces a cyclic monomer into a copper polyacrylate resin to prepare a main-chain degradable self-polishing resin material having polyester chain segments at the main chain and copper ester bonds at the side chain; in the obtained resin not only the copper ester bonds at the side chain can be hydrolyzed but also the polyester chain segments at the main chain can be degraded under seawater attack, thereby solving the problem of the dependence of the traditional self-polishing material on the navigational speed; the coating surface is self-updated in static seawater due to a hydrolytic degradation effect, such that an antifouling agent can be effectively controlled to be released at a constant speed, the retention of active substances on the coating surface of ships or marine equipment is guaranteed, and the anti-fouling requirements of ships at a low navigational speed, offshore production platforms and other facilities are met.

(2) The material provided by the present invention can be evenly and thoroughly polished because the main and side chains can be broken under seawater attack, so that the coating surface maintains a low roughness during the navigation of the ship, thereby reducing sailing resistance and making the material have excellent drag reduction performance.

(3) The present invention can also add different kinds and contents of vinyl monomers in the copolymerization to adjust the glass transition temperature and mechanical properties of the material, and to improve the solubility of the material in the

common solvent of marine coatings as well.

(4) The preparation method provided by the present invention is simple and feasible, has low cost, and is suitable for industrial production; and the prepared copper polyacrylate resin has a good development prospect in the field of marine antifouling coating.

DETAILED DESCRIPTION OF THE EMBODIMENTS

The present invention will be further described below in detail with reference to specific examples, but the embodiments of the present invention are not limited thereto.

Example 1

(1) 64 parts by weight of methyl isobutyl ketone and 16 parts by weight of n-butanol were added to a reaction vessel, and heated to 90℃ in a nitrogen atmosphere; then a mixture composed of 25 parts by weight of stearic acrylate, 40 parts by weight of ethyl methylacrylate, 15 parts by weight of 2-methylene-5-phenyl-1,3-dioxocycloheptane, 20 parts by weight of propenoic acid, 4 parts by weight of di-tert-butyl peroxide, and 2 parts by weight of pentaerythritol tetra(3-mercaptopropionate) was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 58.2 parts by weight of copper propionate, 16.7 parts by weight of acetic acid, and 100 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 130°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin solution).

In this example, the number average molecular weight M_n of the resin was 1.0×10^4 g/mol, the copper content was 13.2%, the acid value was 233 mgKOH/g, and there was no sea creature growth for 12 months indicated by the shallow sea hanging plate test.

Example 2

(1) 64 parts by weight of xylene and 16 parts by weight of propylene glycol methyl ether were added to a reaction vessel, and heated to 95℃ in a nitrogen atmosphere; then a mixture composed of 20 parts by weight of cyclohexyl methylacrylate, 40 parts by weight of isooctyl methylacrylate, 10 parts by weight of hydroxyethyl acrylate, 20 parts by weight of 2-ethyl-2-oxazoline, 10 parts by weight of propenoic acid, 0.02 part by weight of

methanol, and an n-hexane solution of t-BuP_4 (containing 0.04 part by weight of t-BuP_4) was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 11.1 parts by weight of copper oxide, 20.0 parts by weight of isooctanoic acid, and 60 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 140°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin solution).

In this example, the number average molecular weight M_n of the resin was 1.5×10^4 g/mol, the copper content was 6.8%, the acid value was 121 mgKOH/g, and there was no sea creature growth for 10 months indicated by the shallow sea hanging plate test.

Example 3

(1) 80 parts by weight of xylene were added to a reaction vessel, and heated to 100℃ in a nitrogen atmosphere; then a mixture composed of 10 parts by weight of polyethylene glycol methylacrylate (having a degree of polymerization of 9), 10 parts by weight of butyl methylacrylate, 10 parts by weight of 2-methoxyethyl acrylate, 40 parts by weight of acrylate, 20 parts by weight of γ-valerolactone, 10 parts by weight of methylpropenoic acid, 0.01 part by weight of diethylene glycol, and an n-hexane solution of t-BuP_4 (containing 0.04 part by weight of t-BuP_4) was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 11.33 parts by weight of copper hydroxide, 35.1 parts by weight of rosin acid, and 80 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 140°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin).

In this example, the number average molecular weight M_n of the resin was 2.0×10^4 g/mol, the copper content was 5.2%, the acid value was 91 mgKOH/g, and there was no sea creature growth for 8 months indicated by the shallow sea hanging plate test.

Example 4

(1) 64 parts by weight of propylene glycol methyl ether and 16 parts by weight of butyl acetate were added to a reaction vessel, and heated to 100℃ in a nitrogen atmosphere; then a mixture composed of 25 parts by weight of polyethylene glycol methylacrylate (having a degree of polymerization of 9), 40 parts by weight of ethyl acrylate, 30 parts by weight of 2-methylene-1,3-dioxo-4,5-benzocyclopentane, 5 parts by weight of propenoic acid, 2 parts by weight of azobisisobutyronitrile, 2 parts by weight of azobisisovaleronitrile, and 1 part by weight of n-dodecyl mercaptan was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 11.8 parts by weight of copper chloride, 4.2 parts by weight of acetic acid, and 20 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 120°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin solution).

In this example, the number average molecular weight M_n of the resin was 9.5×10^3 g/mol, the copper content was 3.9%, the acid value was 70 mgKOH/g, and there was no sea creature growth for 6 months indicated by the shallow sea hanging plate test.

Example 5

(1) 64 parts by weight of ethyl acetate and 16 parts by weight of acetone were added to a reaction vessel, and heated to 90℃ in a nitrogen atmosphere; then a mixture composed of 10 parts by weight of polyethylene glycol acrylate (having a degree of polymerization of 9), 10 parts by weight of cyclohexyl acrylate, 30 parts by weight of dodecyl methylacrylate, 35 parts by weight of 2-methylene-4-butyl-1,3-dioxocyclohexane, 15 parts by weight of propenoic acid, 4.5 parts by weight of benzoyl peroxide, and 0.5 part by weight of isooctyl 3-mercaptopropionate was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 37.7 parts by weight of copper acetate, 70.8 parts by weight of naphthenic acid (having an acid value of 165), and 150 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 130°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin solution).

In this example, the number average molecular weight M_n of the resin was 1.7×10^4 g/mol, the copper content was 7.2 %, the acid value was 127 mgKOH/g, and there was no sea creature growth for 10 months indicated by the shallow sea hanging plate test.

Example 6

(1) 64 parts by weight of xylene and 16 parts by weight of n-butanol were added to a reaction vessel, and heated to 90℃ in a nitrogen atmosphere; then a mixture composed of 40 parts by weight of ethyl methylacrylate, 20 parts by weight of methyl methylacrylate, 20 parts by weight of δ-valerolactone, 20 parts by weight of methylpropenoic acid, 0.1 part by weight of ethanol, and an n-hexane solution of t-BuP_4 (containing 0.04 part by weight of t-BuP_4) was added dropwise over 3 h; and then the reaction vessel was insulated for 4 h to obtain an acrylate prepolymer;

(2) 42.2 parts by weight of copper acetate, 28.4 parts by weight of benzoic acid, and 100 parts by weight of xylene were added to the acrylate prepolymer of the step (1), and reaction was carried out at 130°C for 8 h to obtain a copper polyacrylate resin (a green transparent resin solution).

In this example, the number average molecular weight M_n of the resin was 1.0×10^4 g/mol, the copper content was 10.3 %, the acid value was 182 mgKOH/g, and there was no sea creature growth for 12 months indicated by the shallow sea hanging plate test done in the Sanya sea area.