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(54) Title: COPOLYMER AND DISPERSANT

(57) Abstract: A novel copolymer and a dispersant using the copolymer are provided. The copolymer is formed of a polyalkylene glycol diester body of itaconic acid, citraconic acid, or mesaconic acid and (meth)acrylic acid. It may further contain other copolymerizable monomer. The copolymer of this invention excels in dispersing property and water-reducing property and manifests a high flow magnitude. Thus, the cement composition using this copolymer enjoys excellent workability when it is put to use.

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DESCRIPTION

COPOLYMER AND DISPERSANT

5 Technical Field

This invention relates to a copolymer of a polyalkylene glycol diester of itaconic acid, citraconic acid, or mesaconic acid and a specific (meth)acrylic acid and a dispersant containing the copolymer.

10 Background Art

Cement is used abundantly at the sites of civil engineering works and building constructions. The cement paste formed by adding water to cement, the mortar formed by adding sand as a fine aggregate thereto, and the concrete
15 formed by further mixing pebbles therewith are used as in structural members, groundsills, and fireproof walls and in large quantities. The cement paste, mortar, and concrete are caused by the reaction of hydration between cement and water to generate strength via coagulation and solidification. As
20 a result, the workability thereof is degraded with the elapse of time after the addition of water. This phenomenon in the raw concrete is generally called a slump loss. The slump loss increases in accordance as the unit amount of water present in the cement paste decreases. Since an addition to the unit
25 amount of water in the raw concrete for the sake of improving the workability results in inducing the concrete, etc. to lose strength, the material necessitating cement and water is required to decrease the amount of water to be used to the fullest possible extent from the viewpoint of strength
30 and durability. Thus, various cement dispersants and water-reducing admixtures are being developed with the object of maintaining the workability without sacrificing the

fluidity in spite of a decrease in the amount of water.

For example, a cement dispersant which is formed of a copolymer obtained by polymerizing an alkoxy polyalkylene glycol mono(meth)acrylic ester type monomer (monomer A) resulting from the transesterification of an alkoxy polyalkylene glycol and (meth)acrylic ester in the presence of a basic catalyst has been known (EP0799807B1). The aforementioned monomer A obtained by the transesterification in the presence of a basic catalyst is rated to excel in commercial superiority because it is capable of substantially enhancing the water-reducing property and substantially reducing the reaction time elapsing till the monomer A is obtained. As the copolymerization component (monomer B), (meth)acrylic acids (salts) are available. Most copolymers used as a cement dispersant adopt the esters of polyalkylene glycols with a polymeric carboxylic acid as their monomers. This adoption resides in utilizing the fact that the relevant copolymer is capable of forming a carboxylic acid with elapse of time owing to the hydrophilic property of the polyalkylene glycol and the hydrolysis with an alkali. As the polymeric carboxylic acid, therefore, such a dicarboxylic acid as itaconic acid may be additionally used in the place of (meth)acrylic acid. In EP0799807B1 mentioned above, as typical examples of the monomer C which can be arbitrarily incorporated, dicarboxylic acids such as maleic acid, fumaric acid, citraconic acid, mesaconic acid, and itaconic acid, and monoesters or diesters of such dicarboxylic acids and uniterminal alkoxy bodies of polyalkylene oxide are cited. In the working examples cited herein, however, no ester of the aforementioned dicarboxylic acid and the uniterminal alkoxy body of polyalkylene oxide was produced as the monomer C.

A concrete admixture which is formed of a vinyl copolymer of an ethylenically unsaturated monomer (monomer A) possessing an oxyalkylene and an alkyl ester monomer (monomer B) of an ethylenically unsaturated mono- or di-carboxylic acid is also disclosed (US000005911820A). The concrete admixture has resulted from a study which was pursued with a view to enabling a hydraulic composition to excel in the ability to retain the fluidity and enhancing the slump retaining property with an insignificant delay of curing. As typical examples of the monomer A, polyalkylene glycol monoallyl ethers and dicarboxylic acid type compounds adding oxyalkylene groups having a carbon number in the range of 2 - 3 such as maleic anhydride, itaconic anhydride, citraconic anhydride, maleic acid, itaconic acid, and citraconic acid are cited besides the esters of uniterminal alkyl hindered polyalkylene glycol and acrylic acid or methacrylic acid. It has a mention to the effect that the other monomer C may be contained besides the monomers A and B mentioned above. As the monomer C, such unsaturated carboxylic acid monomers as acrylic acid are cited. In the working example of the US000005911820A, a copolymer of an EO adduct of maleic acid and methyl acrylate was produced.

As regards the utilization of the hydrophilic property of a polyalkylene glycol, a compound formed by the ester linkage of one molecule of polyalkylene glycol with an itaconic acid monoalkylate having a carbon number in the range of 1 - 22 is used as an emulsifier (US3,689,532). It is disclosed that the compound is prepared by causing an epoxide to act on itaconic acid in the presence of quaternary ammonium and boron fluoride and, when used in combination with boron fluoride, is transformed into a long-chain polyalkylene glycol ester. As concerns the way of producing the ester of itaconic acid and a polyalkylene glycol, a method which resides in reacting

itaconic acid with polyethylene glycol monododecyl ether in the presence of toluene sulfonic acid and a method which resides in reacting itaconic acid with polyethylene glycol monomethyl ether in the presence of 2-chloro-1-methyl pyridinium iodide have been known (Hideyuki Hama et al, Synthesis of Polystyrene/Itaconic acid Long-chain Ester type Graft Copolymer, Science and Industry, pp. 456 - 462, 1994).

Disclosure of the Invention

The conventional dispersants generally contain polyalkylene glycol esters of (meth)acrylic acid and manifest prescribed results in the dispersing property and the water-reducing property. Some of them even contain polyalkylene glycol diesters of dicarboxylic acid such as maleic acid in the place of such monocarboxylic acids as (meth)acrylic acid. The desirability of developing a new dispersant which is further excellent in dispersing property and workability, however, has been finding recognition.

Generally, the dispersant is required not only for the cement but also for coating materials, paper coating agents, binders to be used in molding ceramic sinters, and the like. For the purpose of producing the copolymer to be used in such a wide range, the improvement of the efficiency of production and the excellence of the reaction stability in the process of production are important. Thus, the desirability of developing a novel dispersant which is easy to produce and can be produced in a high yield has been finding approval.

In the light of the true state of affairs mentioned above, this invention is aimed at providing a novel copolymer excelling in dispersing property and water-reducing property.

It is also aimed at providing a dispersant which is easy to produce and excellent in efficiency of production.

The present inventors have made a detailed study concerning monomers heretofore used as a dispersant and copolymers derived therefrom. They have consequently found that copolymers containing a polyalkylene glycol diester of itaconic acid as a monomer component are useful as a dispersant. This invention has been perfected as a result.

It has been heretofore known that the esters of such monocarboxylic acids as (meth)acrylic acid and polyalkylene glycols are used as a dispersant. Since (meth)acrylic acid has low thermal stability, it has not been easily esterified at elevated temperatures. A search for substances excelling in thermal stability has revealed that such dicarboxylic acids as itaconic acid, citraconic acid, and mesaconic acid answer the requirement and that the polyalkylene glycol diesters of these dicarboxylic acids excel in the ability to copolymerize with (meth)acrylic acid.

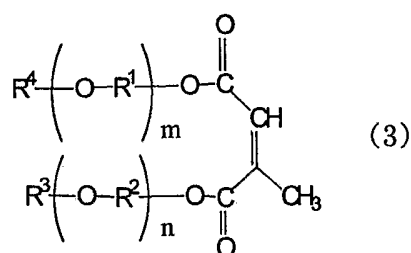
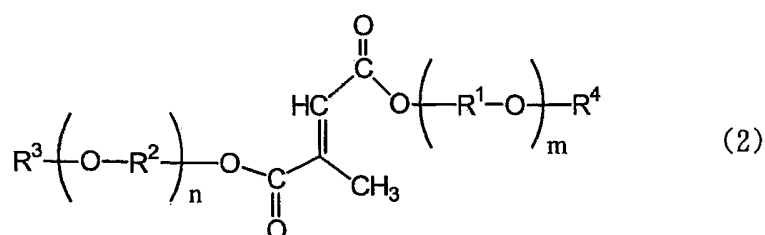
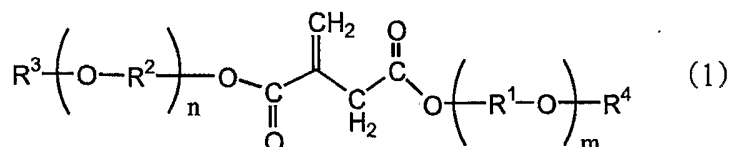
The copolymer of this invention contains the polyalkylene glycol diester of itaconic acid, citraconic acid and/or mesaconic acid as a monomer component and can be ideally used as a dispersant. Particularly, it is capable of uniformly dispersing an inorganic substance or an organic substance which is insoluble in a liquid medium. As a result, it can be used as a cement dispersant, a coating material, a pigment dispersant for a paper coating operation, a dispersant for molding a ceramic sinter, etc.

Moreover, since the monomer excels in thermal stability, it can decrease the amount of the catalyst to be added and can yield the monomer at a high productivity rate.

Best Mode of Embodiment of the Invention

This invention primarily is directed toward a copolymer which is formed by polymerizing a monomer component containing (A) which are any one or more of the monomers represented

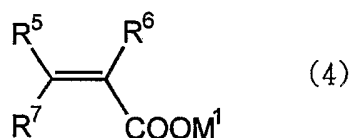
by the following formulas (1) - (3), and (B) which is a monomer represented by the following formula (4)



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wherein $-\text{R}^1\text{O}-$ and $-\text{R}^2\text{O}-$ either identically or not identically denote an oxyalkylene having a carbon number in the range of 2 - 4, m pieces of $-\text{R}^1\text{O}-$ may be identical or not identical, and, when two or more kinds of oxyalkylene are contained, they may be added in a blocked form or a random form, n pieces of $-\text{OR}^2-$ may be identical or not identical, and, when two or more kinds of oxyalkylene are contained, they may be added in a blocked form or a random form, R^3 and R^4 either identically or not identically denote a hydrogen atom, an aliphatic hydrocarbon group having a carbon number in the range of 1 - 20, a substituted or not substituted aryl group or an alkyl group having a carbon number in the range of 6 - 14, m denotes

a number in the range of 1 - 300, and n denotes a number in the range of 1 - 300.



5

wherein R^5 , R^6 , and R^7 either identically or not identically denote a hydrogen atom, methyl, or $-(\text{CH}_2)_p\text{COOM}^2$, the $-(\text{CH}_2)_p\text{COOM}^2$ may form an anhydride with $-\text{COOM}^1$ or another $-(\text{CH}_2)_p\text{COOM}^2$ and, in that case, the groups are devoid of M^1 and M^2 , and M^1 and M^2 either identically or not identically denote a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium, alkylene ammonium, or alkyl ammonium substituted with a hydroxyl group, and p denotes a number in the range of 0 - 2.

15 The foregoing formula (1) represents polyalkylene glycol diesters of itaconic acid and the foregoing formula (2) and formula (3) represent polyalkylene glycol diesters respectively of citraconic acid and mesaconic acid. The citraconic acid and the mesaconic acid are both isomers of
20 itaconic acid. As a polymerizable dicarboxylic acid, maleic acid exists. The copolymer having this polyalkylene glycol diester as a copolymer component is used as a dispersant. As described in the foregoing publication Science and Industry (pp. 456 - 462, 1994), however, the polyalkylene glycol diester
25 of itaconic acid has never been isolated because the reaction of itaconic acid with a polyalkylene glycol forms a monoester body as a main component and this monoester body is separated from the by-produced diester body with difficulty. As a result, the copolymer of the diester body of itaconic acid and
30 (meth)acrylic acid has never been synthesized because the

copolymerizability thereof remains yet to be clarified. The present inventors, by actually synthesizing a polyalkylene glycol diester of itaconic acid, have been ascertained that since the itaconic acid excels in the thermal stability of the double bond thereof, it enables the esterification to proceed at a higher temperature than ever and excels in the yield of the monomer. Further, by investigating the copolymerizability of the monomer with (meth)acrylic acid, they have been ascertained that the monomer possesses high copolymerizability and that the produced copolymer manifests an extremely excellent mortar flow value as compared with the alkylene glycol diester of maleic acid. Now, this invention will be explained in detail below.

The monomer (A) to be used in this invention is represented by the aforementioned formulas (1) - (3). In the formulas (1) - (3), $-R^1O-$ and $-R^2O-$ severally represent an oxyalkylene having a carbon number in the range of 2 - 4. Preferred oxyalkylenes are oxyethylene, oxypropylene, oxytrimethylene, oxyisobutylene, etc. Oxyethylene and oxypropylene are particularly preferable. m pieces of $-R^1O-$ may be identical or not identical. When two or more kinds of oxyalkylene are included, they may be added in a blocked form or in a random form. The same holds good with n pieces of $-OR^2-$. When $-R^1O-$ and $-R^2O-$ both denote oxyethylenes, the monomer excels in dispersing property in an aqueous medium. When m pieces of $-R^1O-$ and n pieces of $-R^2O-$ severally contain an oxypropylene in a ratio in the range of 0 - 30 mol%, preferably in the range of 5 - 25 mol%, and particularly preferably in the range of 10 - 20 mol%, the produced copolymer excels in the balance between the water-solubility and the hydrophobic property.

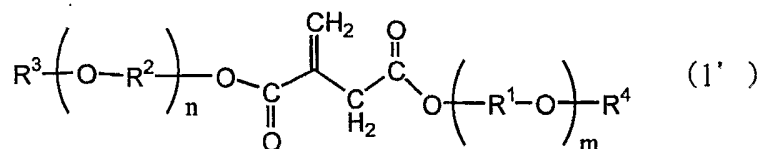
The aliphatic hydrocarbon groups of carbon numbers of 1 - 20 denoted by R^3 and R^4 include branched alkyl groups such

as isopropyl, sec-butyl, tert-butyl, and 2-methyl octane and alicyclic hydrocarbons such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl besides linear alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, 5 octyl, tetradecyl, and octadecyl. The substituted or unsubstituted aryl groups of a carbon number of 6 - 14 include phenyl, o-, m-, or p-tolyl, 2,3- or 2,4-xylyl, cumenyl, mesityl, naphthyl, antholyl, phenanthryl, biphenyl, and pyrenyl. The substituted or unsubstituted aralkyl groups of carbon number 10 of 6 - 14 include benzyl, phenethyl, benzhydryl, and trityl. In this invention, R^3 and R^4 severally denote preferably hydrogen, an alkyl group of a carbon number of 1 - 20, an alicyclic hydrocarbon of a carbon number of 1 - 20, and a substituted or unsubstituted aryl group or aralkyl group of 15 a carbon number of 6 - 14 and more preferably a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and benzyl.

m and n severally denote the degree of polymerization of an alkylene oxy, m is in the range of 1 - 300, preferably 1 - 150, more preferably 4 - 150, further preferably 4 - 100, 20 and particularly preferably 4 - 50 and n is in the range of 1 - 300, preferably 1 - 150, more preferably 4 - 50, further preferably 4 - 100, and particularly preferably 4 - 50. If they deviate from the ranges specified above, the deviation will possibly result in lowering the polymerizability and 25 lowering the dispersing property as well.

In this invention, the monomer (A) may properly adopt any of the aforementioned monomers of the formulas (1) - (3). It does not need to adopt any one of them exclusively but may adopt two or more of them together. Incidentally, the 30 polyalkylene glycol diester of itaconic acid proves favorable since it excels in copolymerizability with the monomer (B). It is the monomer represented by the following formula (1')

that proves particularly favorable.



5 wherein $-\text{R}^1\text{O}-$ and $-\text{R}^2\text{O}-$ each denote an oxyethylene or an oxypropylene, m pieces of $-\text{R}^1\text{O}-$ and n pieces of $-\text{R}^2\text{O}-$ severally contain 0 - 30 mol% of oxypropylene, R^3 and R^4 either identically or not identically denote a hydrogen atom, an aliphatic hydrocarbon group of a carbon number of 1 - 20, or a substituted
10 or unsubstituted aryl group or an alkyl group of a carbon number of 6 - 14, m denotes a number of 1 - 300, and n denotes a number of 1 - 300.

The monomer (B) to be used in this invention is represented by the foregoing formula (4). In the formula (4), M^1 and M^2
15 each denote a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium, an alkyl ammonium, or an alkyl ammonium substituted with a hydroxyl group. Sodium and potassium are preferred alkali metal atoms, magnesium and calcium are preferred alkaline earth metal atoms, methyl
20 ammonium, ethyl ammonium, dimethyl ammonium, diethyl ammonium, propyl ammonium, n-butyl ammonium, sec-butyl ammonium, and tert-butyl ammonium are preferred alkyl ammoniums, and hydroxymethyl ammonium, hydroxyethyl ammonium, hydroxydimethyl ammonium, hydroxydiethyl ammonium,
25 hydroxy-propyl ammonium, hydroxy-n-butyl ammonium, hydroxy-sec-butyl ammonium, and hydroxy-tert-butyl ammonium are preferred alkyl ammoniums substituted with a hydroxyl group. This invention prefers M^1 and M^2 each to be a hydrogen atom, sodium, or potassium.

The $-(CH_2)_pCOOM^2$ which is defined by R^5 , R^6 , and R^7 include sodium salt and potassium salt of carboxyl besides the carboxyl; and anhydrides with other $-COOM^1$. Incidentally, when M^1 and/or M^2 is an alkaline earth metal atom in the foregoing formula (4), the $COOM^1$ may form a salt with other $-(CH_2)_pCOOM^2$. In this case, M^2 is not present. R^5 , R^6 , and R^7 are each preferred to be a hydrogen atom or methyl.

As typical examples of the monomer (B) which is used in this invention, unsaturated monocarboxylic acids such as acrylic acid and methacrylic acid, unsaturated dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid, mesaconic acid, and citraconic acid, and anhydrides thereof, and further salts of these unsaturated carboxylic acids and unsaturated dicarboxylic acids such as, for example, alkali metal salts, alkaline earth metal salts, ammonium salts, alkyl ammonium salts, and alkyl ammonium salts substituted with a hydroxyl group may be cited. One or more members selected from among acrylic acid, methacrylic acid, and sodium salts and calcium salts thereof are particularly preferred examples of the monomer (B).

The compositional ratio of the monomer (A) and the monomer (B) mentioned above for obtaining the copolymer contemplated by this invention does not need to be particularly restricted but may be properly selected to suit the purpose of use of the copolymer. When the copolymer is used as a dispersant, for example, the monomer (A) is in a proportion of 0.5 - 99.5 mol% and the monomer (B) in a proportion of 0.5 - 99.5 mol%, preferably the monomer (A) in a proportion of 3 - 85 mol% and the monomer (B) in a proportion of 15 - 97 mol%, and more preferably the monomer (A) in a proportion of 5 - 70 mol% and the monomer (B) in a proportion of 30 - 95 mol%, on the assumption that the total of the monomer (A) and the monomer

(B) is 100 mol%.

The copolymer of this invention is allowed to contain further another monomer (C) which is copolymerizable with the monomer (A) or the monomer (B). As typical examples of this monomer (C), half esters of unsaturated dicarboxylic acids such as maleic acid mono(methoxypolyethylene glycol) esters and itaconic acid mono(methoxypolyethylene glycol) esters; (meth)acrylic acid alkyl esters such as methyl (meth)acrylate and ethyl (meth)acrylate; (meth)acrylic acid hydroxyalkyl esters such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; and styrene, acrylamide, 2-hydroxy-3-allyloxy-1-propane sulfonic acid and sodium salts thereof may be cited.

The amount of the aforementioned monomer (C) to be incorporated does not need to be restricted but may be properly selected to suit the purpose of use. In this case, the monomer (C) may be incorporated in an amount of not more than 40 mol% on the assumption that the total of the aforementioned monomer (A), monomer (B), and monomer (C) is 100 mol%. Preferably, the aforementioned monomer (A) is in the range of 0.5 - 99 mol%, the aforementioned monomer (B) in the range of 0.5 - 99 mol%, and the aforementioned monomer (C) in the range of 0.5 - 40 mol%, more preferably the aforementioned monomer (A) in the range of 4 - 80 mol%, the aforementioned monomer (B) in the range of 20 - 90 mol%, and the aforementioned monomer (C) in the range of 6 - 30 mol%, and particularly preferably the aforementioned monomer (A) in the range of 5 - 70 mol%, the aforementioned monomer (B) in the range of 30 - 80 mol%, and the aforementioned monomer (C) in the range of 15 - 30 mol% (providing that the total amount of the monomers (A) + (B) + (C) is 100 mol%). If they are shown by mass%, when the total of the monomer (A), the monomer (B) and the monomer

(C) is 100 mass%, the monomer (A) is preferably 55-95 mass%, especially preferable 65-90 mass%. By copolymerizing these monomers in the amounts falling in the respective ranges, it is made possible to obtain the copolymer which excels in dispersibility. Incidentally, the copolymer of this invention which is obtained by polymerizing the aforementioned monomers does not need to be restricted to the method of production which is disclosed by this invention. It is only required to contain the component units originating in the aforementioned monomers. The expression "component units originating in the aforementioned monomers" refers to the configuration (-C-C-) in which the polymerizing double bond (C = C) of each of the monomers is opened by the polymerization reaction.

The copolymer of this invention can be used in its unaltered form as a varying dispersant. It may be dissolved in a solvent such as water and used in the form of an aqueous solution. Though the concentration of the copolymer in the aqueous solution may be properly selected to suit the use and the molecular weight of the polymer, it is generally in the range of 5 - 60 mass%.

The objects for which the dispersant is intended are cement, coating material, paper manufacture, pigment, molding of ceramic sinter, etc. The copolymer is particularly useful for cement dispersant.

When the dispersant is used as a cement dispersant, it may be used together with other cement admixture. As typical examples of the admixture, the AE agent, water-reducing admixture, AE water-reducing admixture, high-performance water-reducing admixture, high-performance AE water-reducing admixture, retarding agent, fluidizing agent, shrinkage-reducing agent, defoaming agent, etc. which are

enumerated in Chapter 4 of "Handbook of Concrete Admixtures (published by N.T.S. K.K. on April 23, 2004)" may be cited. Though the amount of such an admixture to be incorporated can be decided in view of the performance to be expected,
5 it is preferably in the range of 0 - 50 mass% based on 100 mass% of the copolymer of this invention.

When the cement dispersant using the polymer thus obtained as a main component is compounded in a cement composition formed of at least cement and water, it promotes
10 the dispersion of cement. The cement dispersant of this invention can be used for hydraulic cements such as portland cement, cement of high belite content, alumina cement, and various mixed cement and hydraulic materials other than cement such as gypsum.

15 The cement dispersant to be used in this invention manifests an excellent effect even when it is added in a small amount as compared with the conventional cement dispersant. When it is used for mortar or concrete using a hydraulic cement, for example, it is only required to be added during the course
20 of kneading in an amount computed to account for a ratio in the range of 0.02 - 3.0% and preferably 0.1 - 2.0%, based on the mass of cement. This addition results in bringing various favorable effects such as accomplishing a high water-reducing ratio, enhancing the ability to prevent slump
25 loss, reducing the unit amount of water, exalting strength, and enhancing durability. If the amount of the addition falls short of 0.02%, the shortage will prevent the performance from being manifested sufficiently. Conversely, if this amount exceeds 30%, the overage will prove disadvantageous
30 from the economic point of view because the effect thereof substantially reaches its ceiling.

The cement composition formed of the aforementioned

cement dispersant, cement, and water does not need to restrict particularly the amount of cement to be used and the unit amount of water per 1 m³ of the composition. The unit amount of water is in the range of 150 - 190 kg/m³ and the water/cement mass ratio is in the range of 0.10 - 0.65. Preferably, the unit amount of water is in the range of 160 - 185 kg/m³ and the water/cement mass ratio is in the range of 0.2 - 0.5. The cement composition, when necessary, incorporates therein sand and aggregate such as small pebbles.

10 The monomer (A) to be used in this invention may be produced by any method available at all. The monomer represented by the aforementioned formula (1) is preferred to be synthesized by Method 1: the reaction of esterification of itaconic acid or itaconic anhydride and a polyalkylene glycol, Method 2: the reaction of esterification of an itaconic alkylate and a polyalkylene glycol, Method 3: the addition of an alkylene oxide to itaconic acid, and Method 4: the addition of an alkylene oxide to an itaconic acid hydroxyalkyl ester. Incidentally, the compounds represented by the
15 aforementioned formulas (2) and (3) can be similarly synthesized by using citraconic acid and mesaconic acid in the place of itaconic acid.
20

Method 1: Reaction of esterification of itaconic acid or itaconic anhydride and a polyalkylene glycol.

25 The polyalkylene glycols available for this reaction are required to be transformed by the reaction of esterification with itaconic acid or itaconic anhydride into compounds represented by the aforementioned formula (1) and they are varied in a wide range. As typical examples of
30 the polyalkylene glycol of this description, polyalkylene glycols such as polyethylene glycol, polypropylene glycol, ethylene oxide-propylene oxide random copolymer, and ethylene

oxide-propylene oxide block copolymer; uniterminal alkoxy bodies of polyalkylene glycol such as monomethoxypolyethylene glycol, monoethoxypolyethylene glycol, monobutoxypolyethylene glycol, monomethoxypolypropylene glycol, and uniterminal alkyl bodies of ethyleneoxide-propylene oxide random copolymer; uniterminal aryloxy bodies of polyalkylene glycol such as monophenoxypolyethylene glycol, monophenoxypolyethylene glycol, monophenoxy-polyethylene glycol, monophenoxypolypropylene glycol, and uniterminal body of ethylene oxide-propylene oxide random copolymer; and uniterminal aryl alkoxy bodies such as monobenzyloxyethylene glycol, monobenzyloxypolyethylene glycol, monobenzyloxypoly-ethylene glycol, monobenzyloxypolyethylene glycol, monobenzyloxypolypropylene glycol, and uniterminal benzyloxy body of ethylene oxide-propylene oxide random copolymer may be cited. Incidentally, when the ethylene oxide-propylene oxide copolymer is used, it is preferred to contain 1 - 30 mol% of propylene oxide. This invention uses preferably the uniterminal alkoxy body of polyalkylene glycol, the uniterminal aryloxy body of polyalkylene glycol, or the uniterminal aryl alkoxy body of polyallylene glycol and more preferably the uniterminal alkoxy body of polyalkylene glycol from the viewpoint of the excellence in reactivity and the excellence of the dispersibility of the copolymer to be obtained.

Though the amount of the polyalkylene glycol to be incorporated per mol of itaconic acid or itaconic anhydride is theoretically 2 mols, it is preferably in the range of 1.5 - 2.5 mols, more preferably in the range of 1.7 - 2.1 mols, and particularly preferably in the range of 1.8 - 2.0

mols. If this amount falls short of 1.5 mols, the shortage will possibly result in increasing the mixing ratio of itaconic acid and polyalkylene glycol monoester and degrading the dispersibility of the produced copolymer. Conversely, if
5 this amount exceeds 2.5 mols, the overage will prove disadvantageous economically because it brings only a small change in the yield of itaconic acid polyalkylene diester.

The reaction is allowed to use an esterifying catalyst. The catalysts available for the reaction include such sulfonic
10 acid type compounds as toluene sulfonic acid and methyl sulfonic acid. At least one compound selected from the group consisting of phenothiazine, N-oxyl compound, phenol compound, manganese salts such as manganese acetate, copper salts of dialkyl dithiocarbamic acid such as copper
15 dibutylthiocarbamate, and nitroso compounds and amine compounds may be used for the purpose of preventing itaconic acid from being polymerized. Since the thermal stability is high, the production can be accomplished without using this compound. When the compound is used at all, it may be used
20 in the smallest possible amount. For example, it may be not more than 200 ppm based on the total mass of itaconic acid and polyalkylene glycol.

The reaction may be carried out in the presence of a solvent such as benzene, toluene, xylene, or cyclohexane.
25 The reaction ideally proceeds when the reaction substrate concentration (the total amount of itaconic acid or itaconic anhydride and polyalkylene glycol) in the solvent is in the range of 50 - 98 mass% and more preferably in the range of 70 - 95 mass%. The synthesis of a polyalkylene glycol ester
30 of itaconic acid has been tried heretofore, though with an extremely low yield. In the publication Science and Industry (PP 456-462, 1994), for example, the reaction of itaconic

acid with polyethylene glycol monododecyl ether by the use of toluene sulfonic acid as a catalyst failed to produce the target diester body in a high yield and the use of 2-chloro-1-methyl pyridinium iodide in the place of toluene sulfonic acid resulted in producing a monoester body as a main component. Though the cause for this low yield remains yet to be elucidated, it may be logically explained by a supposition that owing to the use of benzene in a large amount as an azeotropic solvent, the reaction temperature was elevated barely to the neighborhood of 120°C and consequently the yield was low. This invention has originated in the particular notice directed to the excellence of itaconic acid in thermal stability and culminated in the discovery that the temperature of esterification can be set at a higher level than ever and the yield can be enhanced by limiting the amount of the solvent in the range mentioned above. Incidentally, the product of publication Science and Industry (PP 456-462, 1994) has a monoester body and a diester body existing in a mixed state. The polyalkylene glycol diester body of itaconic acid, however, has not been substantially isolated from this product because these two bodies do not permit easy separation.

The reaction temperature is in the range of 50° - 220°C, preferably in the range of 100° - 200°C, and particularly preferably in the range of 130° - 180°C. The polyalkylene glycol ester of (meth)acrylic acid has low thermal stability. When the reaction temperature surpasses 130°C, the reaction solution suffers the viscosity thereof to rise after the start of polymerization, with the possible result that the solution will allow no easy agitation any longer and incur a decline in the yield. The itaconic acid, however, excels in thermal stability and enables the temperature to be elevated to the

range mentioned above and permits the esterification to be accomplished within a short time in a high yield. If the temperature falls short of 50°C, the shortage will suffer the reaction to consume an unduly long time. Conversely if this
5 temperature exceeds 220°C, the overage will be at a disadvantage in not allowing the reaction to be accelerated any further. As this reaction of esterification advances, it by-produces water. When this reaction is continued while the water is expelled by distillation, it gives rise to the
10 polyalkylene glycol diester of itaconic acid.

Method 2: The reaction of transesterification of itaconic alkylate and polyalkylene glycol

The polyalkylene glycol to be used in this reaction is required to be transformed by the reaction of
15 transesterification with an itaconic alkylate into a compound represented by the aforementioned formula (1). It is varied in a wide range. The polyalkylene glycols cited in the Method 1 mentioned above can be advantageously used.

As the itaconic alkylate, the diester bodies of itaconic
20 acid and alcohols having carbon numbers of 1 - 8 can be favorably used. As typical examples of the itaconic alkylate, itaconic dimethyl ester, itaconic diethyl ester, itaconic dipropyl ester, itaconic methylethyl ester, and itaconic methylpropyl ester may be cited.

25 Though the amount of the polyalkylene glycol to be incorporated per mol of itaconic dialkylate is theoretically 2 mols, it is preferably in the range of 1.5 - 2.5 mols, more preferably in the range of 1.7 - 2.1 mols, and particularly preferably in the range of 1.5 - 2.0 mols. If this amount
30 falls short of 1.5 mols, the shortage will prevent the transesterification from proceeding sufficiently. Conversely, if this amount exceeds 2.5 mols, the overage will

bring only a small change in the yield of the itaconic polyalkylene glycol diester.

The reaction can be carried out in the presence of such a solvent as benzene, toluene, xylene, or cyclohexane. The
5 reaction ideally proceeds when the reaction substrate concentration (the total amount of itaconic dialkylate and polyalkylene glycol) in the solvent is in the range of 50 - 98 mass% and more preferably in the range of 70 - 95 mass%.

The reaction may use an acidic catalyst or a basic catalyst.
10 Preferably, however, the basic catalyst is used because the copolymer using the produced diester body excels in dispersibility. As typical examples of the preferred basic catalyst, alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, and lithium hydroxide; alkaline earth
15 metal hydroxides such as calcium hydroxide and magnesium hydroxide; alkali metal alkoxides such as sodium methoxide, sodium ethoxide, sodium isopropoxide, potassium methoxide, potassium ethoxide, and potassium isopropoxide; and strongly
20 basic ion-exchange resins having an ammonium salt type amine as an exchange group may be cited. In these basic catalysts, the alkali metal hydroxides and the metal alkoxides prove preferable and sodium hydroxide and sodium methoxide prove particularly preferable. The amount of the basic catalyst to be used is preferably in the range of 0.05 - 5 mass% and
25 particularly preferably in the range of 0.1 - 2.0 mass%, based on the mass of the itaconic alkylate. If this amount falls short of 0.05 mass%, the shortage will prevent the effect of catalysis from being manifested sufficiently. If this amount exceeds 0.5 mass%, the overage will prove only
30 uneconomical. The basic catalyst can be added to the reaction system either all at once or continuously or piecemeal. The addition made continuously or piecemeal proves preferable

from the viewpoint of preventing the surface of catalyst from being inactivated within the system or the catalytic action from being deactivated.

The reaction temperature is preferably in the range of 50° - 220°C, more preferably in the range of 100° - 200°C, and particularly preferably in the range of 100° - 190°C. If this reaction temperature falls short of 50°C, the shortage will suffer the reaction to require an unduly long time. Conversely, if the temperature exceeds 220°C, the overage will be at a disadvantage in preventing the ratio of esterification from being increased any further. The reaction of transesterification can be carried out either batchwise or continuously. In the batchwise reaction, for example, when the bulk temperature is gradually elevated till it reaches the allowable limit, the termination of the reaction is confirmed by the cessation of the flowage of an alkyl alcohol. Then, the polyalkylene glycol diester of itaconic acid aimed at by the reaction is obtained by expelling the itaconic alkylate as an unaltered raw material by distillation under a vacuum. Incidentally, also in this method, the diester can be produced in a short time in a high yield because itaconic acid excels (meth)acrylic acid in thermal stability.

Method 3: Addition of alkylene oxide to itaconic acid

The alkylene oxide to be added to itaconic acid is an alkylene oxide having a carbon number in the range of 2 - 4. As typical example of the alkylene oxide, ethylene oxide, propylene oxide, trimethylene oxide, and isobutylene oxide may be cited. Preferably, ethylene oxide or propylene oxide is used alone or ethylene oxide and propylene oxide are used in combination.

The amount of the alkylene oxide to be added to 1 mol of itaconic acid is theoretically $m + n$ mol. It is preferably

in the range of 2 - 400 mols, more preferably in the range of 8 - 200 mols, and particularly preferably in the range of 16 - 130 mols. In this case, when propylene oxide is additionally used, it is preferable to use the propylene oxide
5 in an amount in the range of 1 - 30 mol%.

The reaction is allowed to use a catalyst. As typical examples of the preferred catalyst, quaternary ammonium compounds, boron fluoride, sodium hydroxide, and potassium hydroxide may be cited. Among other catalysts enumerated
10 above, boron fluoride proves ideal because it is capable of efficiently promoting the non-aqueous reaction.

As typical examples of the quaternary ammonium compound,
4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl
morpholinium chloride,
15 4-(4,6-diethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium
chloride, 4-(4,6-dipropoxy-1,3,5-triazin-2-yl)-4-methyl
morpholinium chloride,
4-(4,6-diisopropoxy-1,3,5-triazin-2-yl)-4-methyl
morpholinium chloride,
20 4-(4,6-dibutoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium
chloride, 4-(4,6-biphenoxy-1,3,5-triazin-2-yl)-4-methyl
morpholinium chloride,
4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-ethyl morpholinium
chloride, 4-(4,6-diethoxy-1,3,5-triazin-2-yl)-4-ethyl
25 morpholinium chloride,
4-(4,6-dipropoxy-1,3,5-triazin-2-yl)-4-ethyl morpholinium
chloride, 4-(4,6-diisopropoxy-1,3,5-triazin-2-yl)-4-ethyl
morpholinium chloride,
4-(4,6-dipropoxy-1,3,5-triazin-2-yl)-4-ethyl morpholinium
30 chloride, 4-(4,6-diisopropoxy-1,3,5-triazin-2-yl)-4-ethyl
morpholinium chloride,
4-(4,6-dibutoxy-1,3,5-triazin-2-yl)-4-ethyl morpholinium

chloride, 4-(4,6-biphenoxy-1,3,5-triazin-2-yl)-4-ethyl
morpholinium chloride,
4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-isobutyl
morpholinium chloride,
5 4-(4,6-diethoxy-1,3,5-triazin-2-yl)-4-isobutyl
morpholinium chloride,
4-(4,6-dipropoxy-1,3,5-triazin-2-yl)-4-isobutyl
morpholinium chloride,
4-(4,6-diisopropoxy-1,3,5-triazin-2-yl)-4-isobutyl
10 morpholinium chloride,
4-(4,6-dibutoxy-1,3,5-triazin-2-yl)-4-isobutyl
morpholinium chloride, and
4-(4,6-biphenoxy-1,3,5-triazin-2-yl)-4-methyl
morpholinium chloride may be cited.

15 By using a quaternary ammonium compound and boron
fluoride in combination, it is made possible to increase the
degree of polymerization of polyalkylene oxide up to a long
chain of 300.

The reaction temperature is preferably in the range of
20 40° - 220°C, more preferably in the range of 100° - 200°C, and
particularly preferably in the range of 100° - 150°C. If the
reaction temperature falls short of 40°C, the shortage will
suffer the reaction to consume an unduly long time. Conversely,
if this temperature exceeds 220°C, the overage will be at a
25 disadvantage in possibly inducing a polymerization reaction.
The reaction time of 2 - 20 hours suffices to produce the
polyalkylene glycol diester of itaconic acid. This reaction
is at an advantage in enabling the target product to be easily
isolated because it can be effectively carried out without
30 requiring use of a solvent. Also in this method, the diester
can be produced in a short time in a high yield because itaconic
acid excels (meth)acrylic acid in thermal stability.

Method 4: Addition of alkylene oxide to itaconic hydroxyalkyl ester

The itaconic hydroxyalkyl ester to be used for this method is an ester body of itaconic acid and a monohydroxy alcohol
5 possessing a linear chain or a branched chain having a carbon number in the range of 2 - 4. Such diester bodies as hydroxy ethanol and hydroxy butanol are preferred examples.

When an alkylene oxide and itaconic hydroxyalkyl ester are mixed, since the itaconic hydroxyalkyl ester functions
10 as a polymerization initiator, the oxyalkylene is polymerized with the hydroxyl group of the itaconic hydroxyalkyl ester. As a result, the produced polyalkylene glycol diester body of itaconic acid has a hydroxyl group as the terminal thereof. For the reaction, such catalysts as quaternary ammonium
15 compounds, boron fluoride, and sodium hydroxide which have been enumerated in the aforementioned Method 3 are favorably usable.

The reaction temperature is preferably in the range of 40° - 220°C, more preferably in the range of 100° - 200°C, and
20 particularly preferably in the range of 100° - 150°C. If this temperature falls short of 40°C, the shortage will suffer the reaction to consume an unduly long time. Conversely, if this temperature exceeds 220°C, the overage will be at a disadvantage in inducing a polymerization reaction. The
25 reaction time in the range of 2 - 20 hours suffices to obtain the polyalkylene glycol diester of itaconic acid. Even in this method, the diester can be produced in a short time in a high yield because itaconic acid excels (meth)acrylic acid in thermal stability.

30 The copolymer of this invention merely requires the monomer component containing the aforementioned monomer (A) and monomer (B) and optionally adding the monomer (C) to be

copolymerized by the use of a polymerization initiator. The copolymerization may be effected by polymerization in a solvent or by a method of bulk polymerization.

The polymerization in a solvent can be carried out either batchwise or continuously. As typical examples of the solvent to be used in the polymerization, water; lower alcohols such as methyl alcohol, ethyl alcohol, and isopropyl alcohol; aromatic or aliphatic hydrocarbons such as benzene, toluene, xylene, cyclohexane, and n-hexane; ester compounds such as ethyl acetate; and ketone compounds such as acetone and methylethyl ketone may be cited. From the viewpoint of the solubility of the raw material monomer and the produced copolymer and the convenience of the copolymer during the course of use, it is preferable to use at least one member selected from the group consisting of water and lower alcohols having carbon numbers of 1 - 4. Among other lower alcohols having carbon numbers of 1 - 4, methyl alcohol, ethyl alcohol, and isopropyl alcohol prove particularly effective.

When the polymerization is carried out in an aqueous medium, a water-soluble polymerization initiator such as a persulfate of ammonium or an alkali metal or hydrogen peroxide is used. In this case, an accelerator such as sodium hydrogen sulfite or Mohr's salt may be additionally used. Then, in the polymerization using a lower alcohol, an aromatic hydrocarbon, an aliphatic hydrocarbon, an ester compound, or a ketone compound as a solvent, peroxides such as benzoyl peroxide and lauroyl peroxide, hydroperoxides such as cumene hydroperoxide; and aromatic azo compounds such as azobisisobutyronitrile can be used as polymerization initiators. In this case, an accelerator such as an amine compound may be additionally used. When a water-lower alcohol mixed solvent is used, the aforementioned various

polymerization initiators and combinations of such polymerization initiators and accelerators are available for proper selection. The polymerization temperature is properly decided, depending on the solvent and the polymerization initiator to be actually used. It is generally in the range of 0° - 120°C.

The bulk polymerization is carried out by using a polymerization initiator selected from among peroxides such as benzoyl peroxide and lauroyl peroxide; hydroperoxides such as cumene hydroperoxide; and aliphatic azo compounds such as azobisisobutyronitrile at a temperature in the range of 50° - 200°C.

Further, for the purpose of adjusting the molecular weight of the produced copolymer, a thiol type chain transfer agent may be additionally used. The weight average molecular weight of the copolymer of this invention is preferably in the range of 4,000 - 80,000, more preferably in the range of 6,000 - 50,000, and particularly preferably in the range of 10,000 - 30,000. If the weight average molecular weight falls short of 4,000, the shortage will possibly result in deteriorating the dispersibility. Conversely, if it exceeds 80,000, the overage will be at a disadvantage in deteriorating the water-reducing property and the slump loss-preventing property of the cement dispersant when the copolymer is used as the cement dispersant. Incidentally, the weight average molecular weight is the magnitude which is obtained by the method of gel permeation chromatography/polyethylene glycol conversion.

Now, this invention will be specifically explained below with reference to the working examples cited herein. These working examples do not restrict this invention in any way. The term "parts" used herein means "parts by mass" unless

otherwise specified.

Synthesis Example 1

(Synthesis of itaconic acid (methoxypolyethylene glycol) ester)

5 In a reaction vessel provided with a nitrogen introducing tube, a thermometer, and a Dean Stark type water separating device, 52 g (0.4 mol) of itaconic acid, 340 g (0.72 mol) of monomethoxypolyethylene glycol (adduct of 10 mols of ethylene oxide of methanol), 0.078 g of phenothiazine, 7.1
10 g of toluene sulfonic acid monohydrate, and 30 g of toluene were placed and heated and stirred under a current of nitrogen. The reaction solution began a reflux when the temperature thereof reached 137°C. When the temperature was further elevated while the removal of the formed water from the reaction
15 vessel was continued, it reached 180°C within 5 hours of starting the reflux. The reaction was completed at this point. The amount of the water so removed totaled 12.0 g (0.67 mol). The ratio of esterification computed from the amount of the removed water was found to be 93%. The subsequent removal
20 of toluene at 160°C under a vacuum resulted in forming 381 g of a reaction mixture (IT-1) having an acid number of 18.3 mgKOH/g and containing 84.1 mass% of itaconic di(methoxypolyethylene glycol) ester and 13.3 mass% of itaconic mono(methoxypolyethylene glycol) ester.

25 Synthesis Example 2

(Synthesis of itaconic di(methoxypolyethylene glycol) ester)

In a reaction vessel provided with a nitrogen introducing tube, a thermometer, and a Dean Stark type water separating
30 device, 42 g (0.32 mol) of itaconic acid, 302 g (0.64 mol) of monomethoxypolyethylene glycol (adduct of 10 mols of ethylene oxide of methanol), 6.2 g of toluene sulfonic acid

monohydrate, and 30 g of toluene were placed and heated and stirred under a current of nitrogen. The reaction solution began a reflux when the temperature thereof reached 147°C. When the temperature was further elevated while the removal
5 of the formed water from the reaction vessel was continued, it reached 185°C within 6 hours of starting the reflux. The reaction was completed at this point. The amount of the water so removed totaled 10.5 g (0.58 mol). The ratio of esterification computed from the amount of the removed water
10 was found to be 91%. The subsequent removal of toluene at 160°C under a vacuum resulted in forming 334 g of a reaction mixture (IT-2) having an acid number of 13.4 mgKOH/g and containing 84.7 weight% of itaconic di(methoxypolyethylene glycol) ester and 8.2 weight% of itaconic
15 mono-(methoxypolyethylene glycol) ester.

Synthesis Example 3

(Synthesis of itaconic di(methoxypolyethylene glycol) ester)

In a reaction vessel provided with a nitrogen introducing
20 tube, a thermometer, and a Dean Stark type water separating device, 21 g (0.16 mol) of itaconic acid, 326 g (0.29 mol) of monomethoxypolyethylene glycol (adduct of 25 mols of ethylene oxide of methanol), 0.035 g of phenothiazine, 5.2 g of toluene sulfonic acid monohydrate, and 60 g of toluene
25 were placed and heated and stirred under a current of nitrogen. The reaction solution began a reflux when the temperature thereof reached 138°C. When the temperature was further elevated while the removal of the formed water from the reaction vessel was continued, it reached 150°C within 19 hours of
30 starting the reflux. The reaction was completed at this point. The amount of the water so removed totalled 3.8 g (0.21 mol). The ratio of esterification computed from the amount of the

removed water was found to be 73%. The subsequent removal of toluene at 160°C under a vacuum resulted in forming 348 g of a reaction mixture (IT-3) having an acid number of 11.9 mgKOH/g and containing 76.9 weight% of itaconic di(methoxypolyethylene glycol) ester and 16.4 weight% of itaconic mono(methoxypolyethylene glycol) ester.

Comparative Synthesis Example 1

(Synthesis of maleic di(methoxypolyethylene glycol) ester)

10 In the same apparatus as used in Synthesis Example 1, 46 g (0.4 mol) of maleic acid, 340 g (0.72 mol) of monomethoxypolyethylene glycol (adduct of 10 mols of ethylene oxide of methanol), 0.072 g of phenothiazine, 6.95 g of toluene sulfonic acid monohydrate, and 30 g of toluene were placed and heated and stirred under a current of nitrogen. The reaction solution began a reflux when the temperature thereof reached 140°C. When the temperature was further elevated while the removal of the formed water from the reaction vessel was continued, it reached 164°C within 2.2 hours of starting the reflux. The reaction was completed at this point. The amount of the water so removed totaled 12.3 g (0.68 mol). The ratio of esterification computed from the amount of the removed water was found to be 95%. The subsequent removal of toluene at 60°C under a vacuum resulted in forming 386 g of a reaction mixture (MA-1) having an acid number of 25.5 mgKOH/g and containing 68.5 weight% of maleic di(methoxypolyethylene glycol) ester and 20.5 weight% of maleic mono(methoxypolyethylene glycol) ester.

Comparative Synthesis Example 2

30 In the same apparatus as used in Synthesis Example 1, 34.4 g (0.4 mol) of methacrylic acid, 170 g (0.36 mol) of monomethoxypolyethylene glycol (adduct of 10 mols of ethylene

oxide of methanol), 3.68 g of toluene sulfonic acid monohydrate, and 16 g of toluene were placed and heated and stirred under a current of nitrogen. When the temperature of the reaction solution reached 125°C, a solid substance which seemed to be
5 a polymer was separated. The reaction was stopped because the separated solid substance did not allow easy stirring any longer.

Example 1

(Synthesis of polymer)

10 In a reaction vessel provided with a nitrogen introducing tube, a condenser, and a stirring device, 8.5 g of IT-1 obtained in Synthesis Example 1, 1.5 g of acrylic acid, 40 g of water, 0.23 g of aqueous 30 mass% sodium hydroxide solution, 0.2 g of ammonium persulfate, and 0.1 g of mercapto propionic
15 acid were placed and heated in an oil bath at 80°C under a current of nitrogen for 2 hours. Subsequently, the resultant solution added 2.45 g of an aqueous 30 mass% sodium hydroxide solution to give rise to an aqueous solution of copolymer (P-1) having a pH value of 6.3. This aqueous solution had
20 a solid content of 19.5 mass%. The weight average molecular weight of P-1 was 14,800.

Example 2

(Synthesis of polymer)

In a reaction vessel provided with a nitrogen introducing
25 tube, a condenser, and a stirring device, 8.5 g of IT-2 obtained in Synthesis Example 2, 1.5 g of acrylic acid, 40 g of water, 0.23 g of an aqueous 30 weight% sodium hydroxide solution, 0.2 g of ammonium persulfate, and 0.1 g of mercapto propionic acid were placed and heated in an oil bath at 80°C under a
30 current of nitrogen for 2 hours. Subsequently, the resultant solution added 2.20 g of an aqueous 30 weight% sodium hydroxide solution to give rise to an aqueous solution of a polymer

(P-2) having a pH value of 6.2. The solid content of this aqueous solution was 19.7 weight% and the weight average molecular weight of P-2 was 22800.

Example 3

5 (Synthesis of polymer)

In a reaction vessel provided with a nitrogen introducing tube, a condenser, and a stirring device, 13 g of water was placed and heated to 60°C under a current of nitrogen. To the water, a solution A formed by mixing 4.38 g of IT-3 obtained
10 in Synthesis Example 3, 3.10 g of an aqueous 20% acrylic acid solution, 0.1 g of mercapto propionic acid, and 5.00 g of an aqueous 0.1N sodium hydroxide solution was added dropwise over a period of one hour and, at the same time, 2.06 g of
an aqueous 5%
15 2,2-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] dihydro-chloride was added dropwise over a period of one hour and 30 minutes. After completion of the dropwise addition, the resultant mixed solution was further heated for one hour and subsequently combined with 0.7 g of an aqueous 30 weight
20 sodium hydroxide solution and 15 g of water to give rise to an aqueous solution of a polymer (P-3) having a pH value of 6.3. The solid content of this aqueous solution was 11.0 weight% and the weight average molecular weight of P-3 was 26000.

25 Comparative Example 1

(Synthesis of polymer)

In a reaction vessel provided with a nitrogen introducing tube, a condenser, and a stirring device, 8.5 g of MA-1 obtained in Comparative Synthesis Example 1, 1.5 g of acrylic acid,
30 40 g of water, 0.23 g of an aqueous 30 weight% sodium hydroxide solution, and 0.2 g of ammonium persulfate and heated in an oil bath at 80°C under a current of nitrogen for 2 hours.

Subsequently, the resultant mixture added 2.53 g of an aqueous 30 weight% sodium hydroxide solution to give rise to an aqueous solution of a polymer (C-1) having a pH value of 6.2. The solid content of this aqueous solution was 22.2 weight% and
5 the weight average molecular weight of C-1 was 31000.

(Evaluation as cement dispersant)

The test of evaluation was performed in accordance with the method for mortar flow test specified in JIS (Japanese Industrial Standard) R5201-1997 by using a kneader of the
10 machine mixing grade specified in the same standard. In the mortar flow test, the magnitude of flow was determined by simply causing a cone to rise and omitting a falling motion. The mortar for the test was composed of 240 g of water, 595 g of ordinary portland cement, and 1350 g of standard sand.
15 Incidentally, the polymer of this invention and the product of Pozorisu Bussan K.K. sold under the trademark designation of MA404 and used herein as a defoaming agent were incorporated in the mortar by having them dissolved in advance in the water used for the composition of the mortar. The amounts of the
20 polymer and the defoaming agent to be added are indicated in Table 1 in weight% based on the weight of the cement.

Table 1

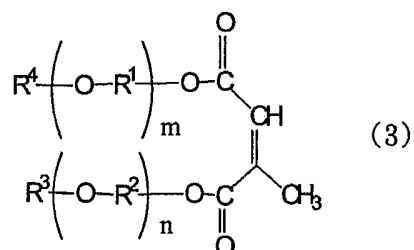
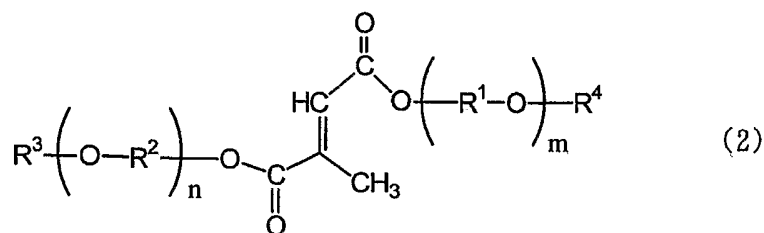
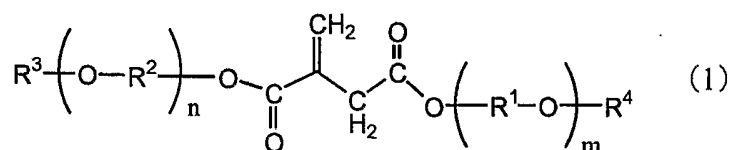
	Polymer	Example 1	Example 2	Example 3	Comparative Example 1
Amount incorporated (%/C)	P-1	0.14			
	P-2		0.14		
	P-3			0.11	
	C-1				0.14
	Defoaming agent	0.01	0.01	0.01	0.01
Magnitude of flow (mm)		197	160	190	105

Industrial Applicability

- 5 The polyalkylene glycol diester of itaconic acid to be used in this invention excels in thermal stability and, therefore, can be produced in a high yield. The copolymer of this diester and (meth)acrylic acid exhibits an excellent dispersibility and is useful as a dispersant.

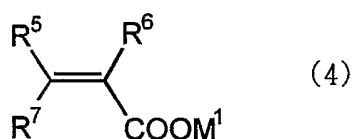
CLAIMS

1. A copolymer formed by polymerizing a monomer component containing (A) which are any one or more of the monomers represented by the following formulas (1) - (3),
 5 and (B) which is a monomer represented by the following formula (4)



- 10 wherein $-\text{R}^1\text{O}-$ and $-\text{R}^2\text{O}-$ either identically or not identically denote an oxyalkylene having a carbon number in the range of 2 - 4, m pieces of $-\text{R}^1\text{O}-$ may be identical or no identical, and, when two or more kinds of oxyalkylene are contained, they may be added in a blocked form or a random form, n pieces
 15 of $-\text{OR}^2-$ may be identical or not identical, and, when two or more kinds of oxyalkylene are contained, they may be added in a blocked form or a random form, R^3 and R^4 either identically

or not identically denote a hydrogen atom, an aliphatic hydrocarbon group having a carbon number in the range of 1 - 20, a substituted or not substituted aryl group or aralkyl group having a carbon number in the range of 6 - 14, m denotes
 5 a number in the range of 1 - 300, and n denotes a number in the range of 1 - 300.



10 wherein R^5 , R^6 , and R^7 either identically or not identically denote a hydrogen atom, methyl, or $-(\text{CH}_2)_p\text{COOM}^2$, the $-(\text{CH}_2)_p\text{COOM}^2$ may form an anhydride with $-\text{COOM}^1$ or another $-(\text{CH}_2)_p\text{COOM}^2$ and, in that case, the groups are devoid of M^1 and M^2 , and M^1 and M^2 either identically or not identically
 15 denote a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, ammonium, alkylene ammonium, or alkyl ammonium substituted with a hydroxyl group, and p denotes a number in the range of 0 - 2.

2. A copolymer according to claim 1, wherein said monomer
 20 (A) is a monomer represented by the formula (1) mentioned above.

3. A copolymer according to claim 1 or claim 2, which contains the monomer (A) and the monomer (B) mentioned above and, when the total of the monomers (A) and (B) mentioned
 25 above is taken as 100 mol%, the monomer (A) is contained in a ratio in the range of 0.5 - 99.5 mol% and the monomer (B) is contained in a ratio in the range of 0.5 - 99.5 mol% in the copolymer.

4. A copolymer according to claim 1 or claim 2, which
 30 further contains another monomer (C) copolymerizable with

said monomer (A) and monomer (B) and, when the total of said monomers (A), (B), and (C) is taken as 100 mol%, the monomer (A) is contained in a ratio in the range of 0.5 - 99 mol%, the monomer (B) in the range of 0.5 - 99 mol%, and the monomer
5 (C) in the range of 0.5 - 50 mol%.

5. A dispersant containing a copolymer set forth in any of claims 1 - 4.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/016863

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. C08F222/20 (2006.01), C04B24/26 (2006.01), C08F220/02 (2006.01), C08F290/06 (2006.01)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int.Cl. C08F222/20 (2006.01), C04B24/26 (2006.01), C08F220/02 (2006.01), C08F290/06 (2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2005 Registered utility model specifications of Japan 1996-2005 Published registered utility model applications of Japan 1994-2005		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WPI/L, CA (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 09-132445 A (KAO CORP) 1997.05.20, Claims, [0019], Examples (No family)	1-5
X A	JP 05-125114 A (EASTMAN KODAK CO) 1993.05.21, Claims, [0011], [0015], Examples & EP 0509327 A1 & US 5190698 A & US 5283008 A	1-4 5
X A	JP 05-045611 A (NIPPON OILS & FATS CO LTD) 1993.02.26, Claims, [0011], Examples (No Family)	1-4 5
X A	JP 05-039322 A (NIPPON OILS & FATS CO LTD) 1993.02.19, Claims, [0012], Examples (No Family)	1-4 5
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date, or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 11.11.2005		Date of mailing of the international search report 22.11.2005
Name and mailing address of the ISA/JP Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		Authorized officer Matsuura Shinji Telephone No. +81-3-3581-1101 Ext. 3457

INTERNATIONALSEARCHREPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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X A	JP 56-020007 A (KYOWA GAS CHEM IND) 1981.02.25, Claims, p.3 upper-left column - upper-right column, Examples (No Family)	1-4 5