

DESCRIPTION

METHOD FOR STOPPING CONTINUOUS POLYMERIZATION

5 TECHNICAL FIELD

[0001]

The present invention relates to a process for discontinuing a continuous polymerization in the continuous polymerization of methacrylate ester polymers and the like.

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BACKGROUND OF THE INVENTION

[0002]

There have been recently adopted continuous bulk polymerization processes or continuous solution polymerization processes in which monomers, a polymerization initiator and the like are continuously added to a polymerization reaction vessel for production of methacrylate ester polymers, acrylate ester polymers, a polystyrene, an acrylonitrile-butadiene-styrene resin (ABS) or the like.

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JP-07-126308A discloses a production of methacrylate ester polymers such as a polymethyl methacrylate (PMMA) by the continuous bulk polymerization process in which methacrylate ester monomers such as methyl methacrylate

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(MMA) and a polymerization initiator are continuously fed in a polymerization reaction vessel.

[0003]

5 When the polymerization reaction of MMA and the like is carried out by the continuous bulk polymerization process, PMMA, a reaction product, is taken out from a reaction vessel as viscous polymerization liquid (hereinafter referred to as "polymerization syrup"), then introduced into,
10 for example, a degas extruder to separate and remove unreacted monomers and further pelletized, for example, by a pelletizer, and provided as a raw material of various PMMA products.

15 [0004]

 At production of the above-mentioned PMMA, when trouble is happened at a degas extruder or a pelletizer which are disposed at the downstream side of a polymerization syrup flow from the reaction vessel, or when inspection and the
20 like are carried out at the above-mentioned downstream side, it is required to stop the influx of polymerization syrup to the downstream side.

[0005]

25 As a method of stopping the influx of polymerization

syrup to the downstream side, there are a method of equipping a storage tank capable of storing polymerization syrup, flowing polymerization syrup into the storage tank capable of storing polymerization syrup, and a method of
5 stopping polymerization reaction at the upstream side.

Since the period capable of stopping the polymerization reaction is dependent on the volume of a storage tank in the method of equipping the storage tank, the storage tank with
10 a large volume are required for an adequate time for inspection, repair and the like, and it is technically very difficult to preserve the polymerization syrup with preventing polymerization in the storage tank. Further, the polymerization syrup collected in the storage tank also can
15 not be reused due to influences of a thermal polymerization and the like at storage.

[0006]

On the other hand, in the method of stopping
20 polymerization reaction at the upstream side, usually, the feed of a polymerization initiator to a polymerization vessel is stopped and the polymerization inhibitor together with an MMA monomer is fed to substitute the inside of the reaction vessel with the MMA monomer containing the
25 polymerization inhibitor. Consequently, a significant time

is necessary for stopping the polymerization reaction through the above procedure, and the influx of much polymerization syrup to the downstream side cannot be immediately stopped when it is necessary. Further, when
5 resuming the polymerization reaction, a substitution of the MMA monomer containing the polymerization inhibitor with a MMA monomer containing a polymerization initiator is required and, a significant time is required for resumption of the polymerization reaction. Furthermore, in this method,
10 temperature increases in reaction vessels might be observed, and the continuous polymerization might not be stably discontinued.

[0007]

15 JP-2006-131847A discloses a method of stopping a continuous polymerization which comprises setting a temperature of a reaction vessel into the specific range by adjusting the supply flow rate of the monomer into the above-mentioned reaction vessel.

20 [0008]

According to this method, a stoppage of prolonged time is possible and the stop and the resumption are easy, but it
25 is necessary to make an operation of adjusting the supply flow rate of the raw monomer depending on a temperature in

the reaction vessel and a temperature of an outer wall of the reaction vessel.

SUMMARY OF THE INVENTION

5 PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

An object of the present invention is to provide a method of stopping a continuous polymerization with a simple operation in which a temperature increase of a content in a reaction vessel can be prevented and the continuous polymerization can be stably stopped, when manufacturing a polymer by the continuous polymerization.

MEANS FOR SOLVING THE PROBLEMS

15 [0010]

The present invention provides a method of stopping a continuous polymerization which comprises continuously supplying a monomer and a polymerization initiator into a reaction vessel to polymerize the monomer in the reaction vessel; and

continuously removing a polymerization composition from an inside of the reaction vessel to an outside of the reaction vessel,

wherein, the method comprises:

25 discontinuing the supply of the polymerization initiator

into the reaction vessel, and
continuously supplying a monomer-containing raw material
having a dissolved oxygen concentration of 0 to 5 ppm into
the reaction vessel at a flow rate in a range of 1/500 to
5 1/10 of a flow rate of a raw material supplied at the
polymerization reaction,
in the state that the stirring in the reaction vessel and
the removal of the polymerization composition to the outside
out of the reaction vessel are continued.

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EFFECTS OF THE INVENTION

[0011]

According to the method of stopping the continuous
polymerization according to the present invention, the
15 stoppage of the polymerization reaction can be smoothly
performed in stopping the polymerization reaction for the
reasons of a trouble occurrence or a check work start.
Moreover, the method of the present invention can prevent
the content temperature increase of the reaction vessel by a
20 simple operation, and can stably discontinue the continuous
polymerization.

BRIEF DESCRIPTION OF DRAWING

[0012]

25 Fig. 1: an example of a continuous bulk polymerization

apparatus used in the present invention.

EMBODIMENTS FOR CONDUCTING THE INVENTION

[0013]

5 The continuous polymerization in the present invention includes a continuous bulk polymerization and a continuous solution polymerization.

[0014]

10 In the present invention, the raw material monomer includes a methacrylate ester monomer, an acrylate ester monomer, styrene, acrylonitrile and the like. The monomer may be used alone or in combination of two or more. Further, rubber polymers such as polybutadiene and SBR can be also used with dissolution.

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[0015]

 Hereinafter, the continuous bulk polymerization using a methacrylate ester monomer as the monomer is illustrated below as an example but it is not limited thereto. The
20 methacrylate ester monomer is not specifically limited, but examples include an alkyl methacrylate, an aryl methacrylate and the like. Among these, an alkyl methacrylate is preferable.

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[0016]

The alkyl in the above-mentioned alkyl methacrylate is not specifically limited, but examples include alkyl having 1 to 18 carbons. Namely, the specific examples of the alkyl methacrylate include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, n-hexyl methacrylate, n-octyl methacrylate, lauryl methacrylate, stearyl methacrylate and the like. Among these, methyl methacrylate is preferable.

[0017]

The above-mentioned methacrylate ester monomer may be used alone or or in combination of two or more.

Further, the polymer obtained by polymerizing the above-mentioned methacrylate ester monomer may be a homopolymer of the methacrylate ester monomer, or may be a copolymer obtained by copolymerizing the monomer which contains at least 50 % by weight of methacrylate ester monomer and at most 50 % by weight of another vinyl monomer copolymerizable therewith. The copolymer is preferably a polymer obtained by copolymerizing the monomer which contains at least 80 % by weight of methacrylate ester monomer and at most 20 % by weight of another vinyl monomer.

[0018]

Examples of the above-mentioned copolymerizable vinyl monomer include acrylate esters such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate and 2-ethylhexyl acrylate; unsaturated carboxylic acids or acid anhydrides such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride and itaconic anhydride; hydroxyl group-containing monomers such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglycerol acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate and monoglycerol methacrylate; nitrogen-containing monomers such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, diacetone acrylamide and dimethylaminoethyl methacrylate; epoxy group-containing monomers such as allyl glycidyl ether, glycidyl acrylate and glycidyl methacrylate; styrene monomers such as styrene and alpha-methyl styrene.

[0019]

The polymerization initiator used in the continuous polymerization in the present invention is selected in accordance with a polymer being an objective or a type of the monomer used for polymerization reaction and is not specifically limited, but for example, radical initiators are mentioned.

[0020]

Examples of the above-mentioned radical initiator
 include azo compounds such as azobisisobutyronitrile,
 5 azobisdimethylvaleronitrile, azobiscyclohexanenitrile, 1,1'-
 azobis(1-acetoxy-1-phenylethane), dimethyl 2,2'-
 azobisisobutyrate and 4,4'-azobis-4-cyanovaleric acid;
 organic peroxides such as benzoyl peroxide, lauroylperoxide,
 acetylperoxide, caproyl peroxide, 2,4-
 10 dichlorobenzoylperoxide, isobutylperoxide,
 acetylcyclohexylsulfonylperoxide, t-butyl peroxy-pivalate, t-
 butyl peroxyneodecanoate, t-butyl peroxyneohexanoate, t-
 butylperoxy-2-ethyl hexanoate, 1,1-di-t-
 butylperoxycyclohexane, 1,1-di(t-butylperoxy)-3,3,5-
 15 trimethylcyclohexane, 1,1-di(t-hexylperoxy)-3,3,5-
 trimethylcyclohexane, isopropylperoxydicarbonate,
 isopropylperoxydicarbonate, isobutylperoxydicarbonate, s-
 butylperoxydicarbonate, n-butylperoxydicarbonate, 2-
 ethylhexylperoxydicarbonate, bis(4-t-
 20 butylcyclohexyl)peroxydicarbonate, t-amylperoxy-2-ethyl
 hexanoate, 1,1,3,3-tetramethylbutylperoxyethyl hexanoate,
 1,1,2-trimethylpropylperoxy-2-ethyl hexanoate, t-
 butylperoxyisopropyl monocarbonate, t-amylperoxyisopropyl
 monocarbonate, t-butylperoxy-2-ethylhexyl carbonate, t-
 25 butylperoxyallyl carbonate, t-butylperoxyisopropyl carbonate,

1,1,3,3-tetramethylbutylperoxyisoproyl monocarbonate, 1,1,2-triamethylpropylperoxyisoproyl monocarbonate, 1,1,3,3-tetramethylbutylperoxyisononate, 1,1,2-trimethylpropylperoxyisononate and tert-butylperoxybenzoate.

5 The polymerization initiator may be used alone or in combination of two or more.

[0021]

The amount of the radical initiator is not specifically
10 limited, but is usually 0.001 to 1% by weight, based on the monomer contained in the raw material. When using two or more of monomers, said amount may be in the above-mentioned range, based on the total amount of the monomers.

15 [0022]

The radical polymerization initiators are not specifically limited, but are preferably compounds whose half-life time at the polymerization temperature is one minute or less. When half-life is less than 1 minute, the
20 reaction velocity is fast so that the polymerization reaction is performed especially satisfactorily.

[0023]

In the continuous polymerization in the present
25 invention, a chain transfer agent may be used for adjusting

the molecular weight of a polymer to be prepared. The above-mentioned chain transfer agent may be either amino-functional chain transfer agent or a poly-functional chain transfer agent, and specific examples include alkyl mercaptans such as propyl mercaptan, butyl mercaptan, hexyl mercaptan, octyl mercaptan, 2-ethylhexyl mercaptan and dodecyl mercaptan; aromatic mercaptans such as phenyl mercaptan and thiocresol; mercaptans having 18 or less of carbon atoms such as ethylene thioglycol; polyhydric alcohols such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol; compounds whose hydroxyl group is esterified with thioglycolic acid or 3-mercaptopropionic acid; 1,4-dihydronaphthalene; 1,4,5,8-tetrahydronaphthalene; beta-terpinen; terpinolene; 1,4-cyclohexadiene; 1,4-cyclohexadiene; hydrogen sulfide and the like. These may be used alone or in combination of two or more.

20 [0024]

Since an amount of the chain transfer agent differs depending on the type of the chain transfer agent to be used, it is not specifically limited, but the amount is preferably 0.01 to 5 parts by weight, based on 100 parts by weight of the monomer contained in the raw material. For example,

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when mercaptans are used, the amount is preferably 0.01 to 3 parts by weight, more preferably 0.05 to 1 part by weight, based on 100 parts by weight of the monomer.

5 [0025]

A mold release agent can be used in the continuous polymerization in the present invention. The mold release agent, although not specifically limited, includes a higher fatty acid ester, a higher aliphatic alcohol, a higher fatty
10 acid, a higher fatty acid amide and a higher fatty acid metal salt. In addition, the mold release agent may be used alone or in combination of two or more. The amount of the mold release agent is preferably adjusted so that the amount is from 0.01 to 1.0 parts by weight, more preferably from
15 0.01 to 0.50 parts by weight, based on the polymerized product (the polymer) 100 parts by weight of the polymer contained in a polymer composition obtained.

[0026]

20 Then, the present invention is illustrated with referring to a continuous bulk polymerization apparatus shown in Fig. 1.

The continuous bulk polymerization apparatus shown in
25 Fig. 1 is equipped with;

a reaction vessel 10,

a stirring blade 11 for stirring contents in the reaction vessel 10,

rotational number detection means 14 for detecting the rotational number of the stirring blade 11,

a monomer feed means (specifically, a monomer feed pump 20) for feeding the raw material monomer to the reaction vessel 10,

an initiator feed means (specifically, an initiator feed pump 25) for feeding a polymerization initiator (or a monomer solution containing the polymerization initiator) (Hereinafter, these may be collectively called as "polymerization initiator and the like") to the reaction vessel 10,

a temperature detection means (specifically, a temperature sensor 35) for detecting temperature in the reaction vessel 10,

a temperature adjustment means (specifically, a jacket 15) for adjusting temperature of the external wall of the reaction vessel 10,

an initiator feed flow rate control means 32 for controlling the flow rate of the polymerization initiator and the like fed to the reaction vessel 10 and for stopping the feed of the polymerization initiator by the initiator feed means (the initiator feed pump 25) when stopping the

polymerization reaction caused by a trouble at the downstream side D of the reaction vessel,

a monomer feed flow rate control means 31 for controlling the flow rate of the raw material monomer fed to the reaction vessel 10 and for controlling the feed flow rate of the raw material monomer by the monomer feed means (the monomer feed pump 20) when the polymerization reaction is stopped because trouble is generated at the downstream side D of the reaction vessel, and

a temperature adjustment and control means 33 for adjusting the setting temperature of the temperature adjustment means (the jacket 15).

[0027]

The continuous bulk polymerization apparatus has: monomer feed tanks 21, 51, and 56, initiator feed tank 26, and mixing vessels 61 and 66 for preparing the raw material monomer (namely, a monomer, or a monomer solution containing an additive agent such as a chain transfer agent and a mold release agent) supplied into the monomer feed tanks. Inert gas introduction lines 21a, 51a, 56a, 26a, 61a, 66a, 71a, and 76a are connected to each of the monomer feed tanks 21, 51, and 56, the initiator feed tank 26, and the mixing vessels 61, 66, 71, and 76.

[0028]

In the continuous bulk polymerization apparatus shown in Fig. 1, the reaction vessel 10 is not specifically limited, but preferably is a perfect mixing type reaction vessel which can form substantially perfect mixing condition in the reaction vessel.

[0029]

10 The stirring blade 11 for stirring contents in the reaction vessel 10 is not specifically limited, but examples include a MIG blade, a MAX BLEND blade (a trade mark; manufactured by Sumitomo Heavy Industries Ltd.), a paddle blade, a double helical blade, a Full Zone blade
15 (manufactured by Shinko Pantec Co., Ltd.) and the like. Preferably, baffles are installed in the reaction vessel in order to improve stirring effect in the reaction vessel.

[0030]

20 The stirring motive energy during the polymerization reaction and the polymerization discontinuation is not specifically limited, but preferably is 0.5 to 30 kW/m³ and more preferably is 1 to 15 kW/m³. The higher the stirring efficiency of the stirring blade 11 is, the more preferable
25 it is. The stirring motive energy is preferably constant

during the polymerization reaction and the polymerization discontinuation. The higher the viscosity of the reaction system is (or the higher the polymer content in the reaction system is), the larger the stirring motive energy is preferably set to be. Preferably, during the polymerization reaction and the polymerization stoppage, the stirring motive energy is almost the same and is kept constant.

[0031]

10 In the present invention, the stirring in the reaction vessel is continuously performed during the polymerization reaction (that is, a polymerization reaction step) and during the polymerization stoppage (that is, a polymerization stoppage step). The stirring blade 11 is
15 equipped with a rotational number detection means 14 for adjusting its rotational number.

The monomer and the polymerization initiator are supplied into the reaction vessel 10 during a polymerization
20 reaction. Said supply is performed by supplying the polymerization raw material which contains the monomer, the polymerization initiator, and, if necessary, the additive agent such as the chain transfer agent and the mold release agent.

In order to stop polymerization, the supply of a polymerization initiator is discontinued. While stopping polymerization by discontinuing the supply of the polymerization initiator, the raw material which contains the monomer and, if necessary, the additive agent such as the chain transfer agent and the mold release agent is supplied into the reaction vessel 10.

[0032]

10 The flow rate of the raw material during the polymerization stoppage is $1/500$ to $1/10$, preferably $1/100$ to $1/25$ of the flow rate of the polymerization raw material during the polymerization reaction. During the polymerization reaction and during the polymerization stoppage, the ingredients of the raw material may be the same except for the presence or absence of the polymerization initiator, and, for example, the amount (or the ratio) of the additive agent in the raw material is preferably the same. Moreover, the supply flow rate of the raw material during polymerization stoppage is preferably constant.

[0033]

25 In the present invention, the raw material having the dissolved oxygen concentration adjusted to 0-5 ppm,

preferably 0-4 ppm, especially 0-3 ppm is supplied into the reaction vessel 10 during the polymerization stoppage. In connection with this, the polymerization composition (that is, a polymerization syrup and the like) containing a resultant polymer and an unreacted monomer is extracted from the reaction vessel 10.

[0034]

The method of adjusting the dissolved oxygen concentration is not limited. Examples of the adjustment method generally include removal of the dissolved oxygen: by introducing the inert gas from an inert gas introduction line into the raw material monomer (that is, the monomer or the monomer solution containing the additive agent) contained in the monomer feed tank or in the mixing vessel for mixing the raw material monomer supplied into the monomer feed tank, whereby bubbling the inert gas; or by a vacuum deaeration. Furthermore, examples of the adjustment method include a mixing method which uses a line mixer. Preferably, motionless mixers such as a static mixer, are used as the line mixer. The line mixer may be installed at the line which supplies the raw material monomer into the mixing vessel or the monomer feed tank, or may be installed at a monomer feed line (piping). The dissolved oxygen in the raw material monomer can be removed by equipping a

gas/liquid separation device, supplying continuously the inert gas into the line mixer, and discharging the inert gas from the gas/liquid separation device. Examples of the inert gas include a nitrogen gas, a helium gas, a neon gas and an argon gas. Preferably, the amount of the inert gas is from 2 to 16 parts by volume, based on one part by volume of the monomer contained in the raw material monomer.

[0035]

The state in the reaction vessel 10 during the polymerization reaction is not specifically limited, but the state in which gas phase is not substantially included (hereinafter, the state is referred to as "full liquid state") is preferable. Problems that gels adhere and grow on the inner wall face of the reaction vessel 10 or that the quality of a polymer is lowered by mixing of the gels can be prevented from occurring, by forming the full liquid state in the reaction vessel 10. Further, when the full liquid state is formed in the reaction vessel 10, the whole volume of the reaction vessel 10 can be effectively utilized for preparation of the polymer; therefore, the production efficiency of the polymer can be improved.

[0036]

With respect to a method for attaining the full liquid

state in the reaction vessel 10, the most convenient method includes a method of arranging a removal outlet 13 for extracting the polymerization syrup out of the reaction system at the uppermost portion of the reaction vessel 10.

5 Further, the pressure in the reaction vessel 10 is adjusted so as to be pressure which is the vapor pressure or more of the monomer at the temperature in the reaction vessel in order not to generate the gas of the monomer in the reaction vessel 10. The pressure is usually about 1 to 2 MPa.

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[0037]

Further, it is preferable that the state in the reaction vessel 10 during the polymerization reaction is an adiabatic state in which the incomings and outgoings of heat
15 does not substantially occur from the external portion of the reaction vessel. In order to let the state in the reaction vessel 10 be an adiabatic state, a temperature in the reaction vessel may be set at nearly equal temperature to that of the external wall, and as a specific means for
20 obtaining the adiabatic state, for example, as described later, temperature adjustment means such as a jacket 15 which can adjust temperature surrounding the external wall of the reaction vessel 10 is mentioned.

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[0038]

Problems that gels adhere and grow on the inner wall face of the reaction vessel 10 or that the quality of a polymer is lowered by mixing of the gels can be prevented from occurring by forming the full liquid state in the reaction vessel 10. Further, by forming the full liquid state in the reaction vessel 10, the polymerization reaction can be stabilized and self controllability for suppressing the excessive reaction can be imparted. However, it is not preferable that the temperature of the external wall of the reaction vessel is set as too high in comparison with temperature in the reaction vessel, because excessive heat is added in the reaction vessel. The less the temperature difference between the inside of the reaction vessel and the external wall of the reaction vessel is, the more preferable it is, and specifically, it is preferable to adjust the temperature within a fluctuation width of about 5 at the stationary state of the polymerization reaction.

[0039]

The polymerization heat and the stirring heat which are generated in the reaction vessel 10 are usually removed when polymerization syrup are extracted. The heat quantity removed by the polymerization syrup is determined by the flow rate of the polymerization syrup, specific heat and the temperature of the polymerization reaction.

[0040]

The temperature in the reaction vessel 10 during the polymerization reaction is fluctuated in accordance with various conditions until being stationary state and is not specifically limited, but is set at preferably about 125 to 200 degrees Celsius, more preferably about 130 to 180 degrees Celsius. When the temperature is extremely high, for example, the syndiotacticity of a polymer obtained is lowered; as a result, fear of lowering the heat resistance property of a resin is generated. Preferably, the temperature in the reaction vessel 10 during the polymerization stoppage is almost the same as the temperature during the polymerization reaction.

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[0041]

The average residential time of the monomer in the reaction vessel 10 during the polymerization reaction is not specifically limited, but is usually 15 minutes to 6 hours, preferably 15 minutes to 3 hours and more preferably 20 minutes to 1.5 hours. When the residential time of the monomer is elongated beyond necessity, the preparation amount of oligomers such as a dimer and a trimer becomes much and there is fear that the heat resistance property of the polymer (methacrylate ester-based polymer) which is a

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reaction product is lowered. The above-mentioned average residential time can be suitably adjusted by changing the feed flow rate of the monomer per a unit time.

5 [0042]

As the monomer feed means, for example, the monomer feed pump 20 for introducing the raw material monomer from a feed orifice 12 to the reaction vessel 10 is mentioned. The monomer feed pump 20 is not specifically limited, but is preferably a pump which can set the feed flow rate of the raw material monomer into the reaction vessel 10 at a predetermined amount. Specifically, multiple-barreled reciprocal pumps such as a double-barreled pump, a triple-barreled pump and a quintuple-barreled pump are preferably mentioned, and non pulsation metering pumps such as a double-barreled non pulsation metering pump, a triple-barreled non pulsation metering pump and a quintuple-barreled non pulsation metering pump are more preferably mentioned.

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[0043]

The feed flow rate of the raw material monomer by the monomer feed pump 20 can be controlled by a monomer feed flow rate control means 31 in a control portion 30 described later and can be suitably adjusted when the residential time

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of the polymerization syrup in the reaction vessel 10 is to be changed.

[0044]

5 As shown in Fig. 1, a monomer feed tank 21 storing the raw material monomer is connected with the feed orifice 12 of the reaction vessel 10 through a monomer feed channel (pipe) 23. The monomer feed pump 20 is positioned at a downstream side from the monomer feed tank 21 when the
10 monomer feed tank 21 is considered as an upstream side and the above-mentioned feed orifice 12 is considered as a downstream side, and is arranged on the above-mentioned monomer feed channel 23.

15 [0045]

 As the initiator feed means, for example, the initiator feed pump 25 for introducing the polymerization initiator and the like from the feed orifice 12 into the reaction vessel 10 is mentioned.

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 The initiator feed pump 25 is not specifically limited, but is preferably a pump which can set the feed flow rate of the polymerization initiator and the like into the reaction vessel 10 at a predetermined amount. Specifically, like the
25 above-mentioned monomer feed pump 20 a multiple-barreled

reciprocal pump is preferably mentioned and a non pulsation metering pump is more preferably mentioned.

[0046]

5 The feed flow rate of the polymerization initiator by the initiator feed pump 25 can be controlled by the initiator feed flow rate control means 32 in the control portion 30 described later. When the polymerization reaction is to be stopped, or when the temperature in the reaction vessel 10 is to be adjusted and the like, it can be
10 suitably adjusted. Further, when the polymerization reaction is to be stopped, the feed of the polymerization initiator and the like is stopped by the initiator feed flow rate control means 32.

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[0047]

 As shown in Fig. 1, an initiator feed tank 26 storing the polymerization initiator and the like is connected with the feed orifice 12 of the reaction vessel 10 through an
20 initiator feed channel (pipe) 28. The initiator feed pump 25 is positioned at a downstream side from the initiator feed tank 26 when the initiator feed tank 26 is considered as an upstream side and the above-mentioned feed orifice 12 is considered as a downstream side, and is arranged on the
25 above-mentioned initiator feed channel 28.

[0048]

Those which are stored in the above-mentioned initiator feed tank 26 and fed into the reaction vessel 10 by the initiator feed means may not be a polymerization initiator alone but may be the monomer solution containing the polymerization initiator (or further containing other components (the additive agent) such as a chain transfer agent).

For example, when the polymerization initiator alone is fed into the reaction vessel 10 by the initiator feed means, there is fear that the polymerization reaction proceeds locally in the reaction vessel 10 depending on condition at feed, but such a problem can be solved by feeding those preliminarily prepared mixture of the polymerization initiator and the monomer into the reaction vessel 10 by the initiator feed means.

[0049]

As shown in Fig. 1, a heating and cooling device 22 for heating or cooling, to a suitable temperature, the above-mentioned polymerization raw material (that is, a first raw material) (which is supplied into during the polymerization reaction (that is, the polymerization reaction step) and which comprises the monomer, the polymerization initiator

and, if necessary, the additive agent such as the chain transfer agent and the mold release agent) or the above-mentioned raw material (that is, a second raw material) (which is supplied during the polymerization stoppage (that is, the polymerization stoppage step) and which contains the monomer and, if necessary, the additive agent such as the chain transfer agent and the mold release agent) to be fed into the reaction vessel 10 is positioned between the above-mentioned feed orifice 12 and a part of joining the above-mentioned monomer feed line 23 and the initiator feed line 28.

[0050]

The temperature of the polymerization raw material fed into the reaction vessel 10 is not specifically limited, but since it may be a factor which collapses heat balance in the reaction vessel and fluctuates polymerization temperature it is preferable to suitably adjust the temperature by the heating and cooling device 22. On the other hand, during the polymerization stoppage, the temperature of the raw material can be set to a low temperature or a high temperature, for example, in order to intentionally decrease or increase, respectively, the supply flow rate of the raw material, because a required supply flow rate is changed also depending on the temperature of the raw material to be

supplied, in the case where the supply flow rate of the raw material is adjusted so that the temperature in a reaction vessel can not be affected, and so that a blockage in the inside of the reaction vessel and piping can not be caused.

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[0051]

As the temperature detection means for detecting the temperature in the reaction vessel, for example, a temperature sensor 35 is mentioned. Examples of the temperature sensor 35 include a temperature sensor which is positioned in the inside of the reaction vessel 10 and can directly detect the temperature of the reaction system stored in the reaction vessel 10, and the like, but the situated position of the temperature sensor and its detection method are not limited thereto.

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[0052]

The temperature in the reaction vessel 10 detected by the above-mentioned temperature detection means (the temperature sensor 35) is transmitted to the control portion described later and becomes data for judging the necessity of controlling feed flow rate by the monomer feed means or the initiator feed means.

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[0053]

As the temperature adjustment means for adjusting the temperature of the external wall of the reaction vessel, for example, a jacket covering the external wall of the reaction vessel, a heater positioned in the reaction vessel and the like are mentioned. Among these, a jacket covering the external wall of the reaction vessel is preferably mentioned from the viewpoint of letting the inside of the reaction vessel be adiabatic state and a jacket 15 covering the nearly whole external wall of the reaction vessel 10 is more preferably mentioned.

[0054]

The jacket 15 shown in Fig. 1 heats or keeps the temperature in the reaction vessel 10 by introducing heating medium such as steam, hot water and organic heating medium from a heating medium feed channel 16. The temperature of the jacket 15 can be suitably adjusted by the temperature or pressure of the heating medium fed. The heating medium introduced into the jacket 15 is removed from a heating medium discharge channel 17. Further, the temperature and pressure of the jacket 15 are detected by a sensor such as a temperature sensor 36 located on the heating medium discharge channel 17. The located positions of the sensor such as the temperature sensor 36 are not specifically limited, but for example, may be on a heating medium feed

channel 16 or in the jacket 15.

[0055]

5 The polymerization reaction in the reaction vessel 10
is preferably carried out with keeping at a nearly constant
temperature from the viewpoint of making the quality of a
polymer prepared be constant. Accordingly, the temperature
adjustment means (the jacket 15) is preferably controlled at
10 a predetermined constant temperature so that the temperature
in the reaction vessel 10 can be kept nearly constant.

[0056]

15 The setting temperature of the above-mentioned
temperature adjustment means (the jacket 15) is transmitted
to the control portion 30 described later and becomes data
for judging the necessity of controlling feed flow rate by
the monomer feedmeans or the initiator feedmeans. When the
above-mentioned temperature adjustment means is the jacket
15, the setting temperature of the temperature adjustment
20 means can be adjusted by controlling the above-mentioned
temperature or pressure of heating medium by the temperature
adjustment and control means 33 described later.

[0057]

25 Examples of the control portion 30 which is a control

means of controlling the feed flow rate of the raw material monomer and the feed flow rates of the polymerization initiator and the like include a control portion equipped with CPU, ROM, RAM and the like.

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[0058]

The ROM of the control portion 30 is a device for storing a program for controlling the monomer feed pump 20 by the monomer feed flow rate control means 31 and for
10 storing a program for controlling the initiator feed pump 25 by the initiator feed flow rate control means 32, and the RAM of the control portion 30 is a device which temporarily stores temperature data in the reaction vessel 10 detected by the temperature sensor 35, the data of setting
15 temperature of the jacket 15 and the data of the rotational number of the stirring blade 11 detected by rotational number detection means 14 in order to perform the above-mentioned program.

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[0059]

The CPU of the control portion 30 performs the program stored in the above-mentioned ROM based on the data stored in the above-mentioned RAM and controls the feed flow rate of the raw material monomer and/or the polymerization
25 initiator into the reaction vessel 10 by the monomer feed

means (the monomer feed pump 20) and/or the initiator feed means (the initiator feed pump 25).

[0060]

5 One example of the controls by the monomer feed flow rate control means 31, the initiator feed flow rate control means 32 and the temperature adjustment and control means 33 in the control portion 30 is shown below.

10 [0061]

 When the polymerization reaction is to be stopped by a trouble generated at the downstream side D of the reaction vessel 10 or inspection and the like, the feed of a polymerization initiator into the reaction vessel 10 is
15 stopped by performing the program in the above-mentioned ROM by the above-mentioned CPU and by controlling the initiator feed pump 25 which is the initiator feed means, with using the initiator feed flow rate control means 32.

20 [0062]

 When a polymerization reaction is stopped, the raw material (containing the monomer) adjusted to have the dissolved oxygen concentration to 0-5 ppm is supplied. Preferably, the raw material is a raw material consisting of
25 the monomer alone or a raw material consisting of the

monomer and the chain transfer agent.

[0063]

During the polymerization stoppage, the raw material
5 may be supplied from the monomer feed line 23;
the raw material may be supplied from the polymerization
initiator feed line 28, in order to prevent the
polymerization initiator from staying in the initiator feed
line when supply of the polymerization initiator and the
10 like is stopped for the stoppage of a polymerization
reaction; or
the raw material may be supplied by supplying the raw
material monomer from both of the monomer feed line 23 and
the initiator feed line 28.

15

[0064]

Although the feed flow rate of the raw material monomer
is greatly reduced at stoppage of the polymerization
reaction as mentioned above, the feed of the raw material
monomer to the reaction vessel 10 is successively carried
20 out; therefore polymerization syrup with an amount
comparable to the feed flow rate are required to be
extracted from the reaction vessel 10.

25

[0065]

The polymerization syrup and the like (namely the polymerization composition) discharged during stoppage of the polymerization reaction are extracted from, for example, the removal outlet 13 of the reaction vessel 10 in the same manner as a conventional treatment method against the polymerization syrup which is prepared during the polymerization reaction and is transferred and collected through a polymerization syrup derivation channel 40.

Since an unreacted raw material monomer is contained in either of the polymerization syrup discharged during stoppage of the polymerization reaction and the polymerization syrup extracted during the polymerization reaction, treatment for evaporating and separating volatile portions in which the unreacted raw material monomer is a main component is carried out, if necessary.

[0066]

As the transfer method of the above-mentioned polymerization syrup and polymerization syrup, a method described in JP-A-04-48802 is preferable. Further, as a method of evaporating and separating the above-mentioned volatile portions, a method using a degas extruder is known and, for example, methods described in JP-A-51-29914 and JP-A-52-17555, JP-B-01-53682, JP-A-62-89719 and JP-A-03-49925

are preferable.

[0067]

When the reaction vessel used in the present invention
5 is a perfect mixing type reaction vessel, a polymerization
rate at which a monomer is converted to a polymer in the
reaction vessel is generally equivalent to a polymer content
rate in the polymerization syrup. In the present invention,
the polymerization rate is not specifically limited, but is
10 usually set at 40 to 70% by weight. The higher the
polymerization rate is, the higher the productivity of a
polymer is; however, the viscosity of the reaction system is
heightened and great stirring motive energy is required.
Further, the lower the polymerization rate, the lower the
15 productivity; therefore load for collecting an unreacted raw
material monomer is enlarged.

[0068]

In the present invention, an unreacted monomer
20 separated and collected from the polymerization syrup is
stored in a monomer collection tank 41 and if necessary, fed
again to the monomer feed tank 21 to be able to be provided
for the polymerization reaction. Further, the unreacted
monomer collected is not limited thereto, but it is
25 preferable that a polymerization inhibitor (for example,

"TOPANOL A" and the like) is let exist at a proportion of 2 to 8 ppm, the oxygen concentration of a gas phase portion is set at 2 to 8% by volume and further, the monomer is stored in cooled state, specifically, at a low temperature of, for example, about 0 to 5 degrees Celsius so that the polymerization reaction does not proceed during stored in a monomer collection tank 41 or the monomer feed tank 21. It can be stored for a long term by being stored thus, while preventing the polymerization reaction of the unreacted monomer collected.

[0069]

During the polymerization stoppage, the raw material having the dissolved oxygen concentration of 0 to 5 ppm may be supplied into the reaction vessel 10:

by adjusting the dissolved oxygen concentration of the raw material monomer in the monomer feed tank 21 to 0-5 ppm according to the above-mentioned adjustment method and supplying said raw material monomer into the reaction vessel 10;

by changing the valve of the junction of the monomer supply line (piping) 23 and the monomer feed line (piping) 53 to connect the monomer feed pump 20 with the monomer feed tank 51 through the monomer feed line (piping) 53, adjusting the dissolved oxygen concentration of the raw material monomer

in the monomer feed tank 51 to 0-5 ppm according the above-mentioned adjustment method, and supplying said raw material monomer into the reaction vessel 10; or

by changing the valve of the junction of the initiator feed

5 line (piping) 28 and the monomer feed line (piping) 58 to connect the initiator feed pump 25 with the monomer feed tank 56 through the monomer feed line (piping) 58, adjusting the dissolved oxygen concentration of the raw material monomer in the monomer feed tank 56 to 0-5 ppm according to

10 the above-mentioned adjustment method, and supplying said raw material monomer into the reaction vessel 10. Moreover, the raw material having the dissolved oxygen concentration of 0 to 5 ppm may be supplied into the reaction vessel 10 by suitably adjusting the dissolved oxygen concentrations in
15 the raw material monomers in the monomer feed tank 21, the raw material monomer in the monomer feed tank 51 and the raw material monomer in the monomer feed tank 56, and adjusting the mixed ratio of the raw material monomers supplied from each of monomer feed tanks so that the mixed raw material
20 supplied into the reaction vessel 10 has the dissolved oxygen concentration of 0-5 ppm.

[0070]

Moreover, another monomer feed tank, a monomer feed
25 line, and a monomer feed pump (not shown) may be equipped so

that the raw material monomer may be supplied from the monomer feed tank to the reaction vessel. In this case, the flow rate of the raw material monomer and the dissolved oxygen concentration in the raw material monomer supplied from the another monomer feed tank may be adjusted so that the dissolved oxygen concentration contained in the total of the raw material supplied in the reaction vessel 10 is set to 0-5 ppm. The dissolved oxygen concentration in the raw material monomer supplied from the another monomer feed tank is preferably from 0 to 5 ppm.

[0071]

When the continuous polymerization of the present invention is a continuous solution polymerization, a solvent is used for the polymerization reaction; in this case, a continuous polymerization apparatus is further equipped with a tank for feeding a solvent, a feeding channel and a pump (feed means).

[0072]

The tanks for feeding a solvent, feeding channel and pump (feed means) are not specifically limited and may be similar as those conventionally used. Further, the solvent may be fed into the reaction vessel after mixing the monomer and/or the polymerization initiator with it, or may be

directly fed into the reaction vessel. As the above-mentioned solvent, solvents described later are mentioned.

[0073]

5 The continuous solution polymerization apparatus is similar as the above-mentioned continuous bulk polymerization apparatus except that a tank for feeding a solvent, a feeding channel, a pump (feed means) and the like are provided.

10

[0074]

Further, the continuous solution polymerization is similarly carried out in the same manner as the above-mentioned continuous bulk polymerization except that a
15 solvent is used for the polymerization reaction. The solvent used for the polymerization reaction is selected, for example, according to the monomer for the continuous polymerization reaction, is not specifically limited, and is generally an organic solvent. Examples of the solvent
20 include an organic solvent having 1 to 20 (for example, 1 to 12) carbon atoms, for example, an aliphatic hydrocarbon, an aromatic hydrocarbon, an araliphatic hydrocarbon, an alcohol, a ketone and an ester. Specific examples of the solvent
25 include toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, octane, decane,

cyclohexane, decalin, butyl acetate and pentyl acetate.

[0075]

5 In the continuous solution polymerization in the present invention, a ratio C : D in which C (kg/hr) is a feed flow rate of the monomer, and D (kg/hr) is a feed flow rate of the solvent, is not limited thereto, but for example, is preferably 2:98 to 50:50, more preferably 5:95 to 30:70.

10 Examples

[0076]

Hereinafter, the present invention is specifically explained by showing Examples.

15 [0077]

In the Examples, measurement was performed as follows.

Dissolved oxygen concentration:

20 A dissolved oxygen concentration was measured by using a dissolved oxygen meter (DO meter OM-51 manufactured by Horiba, Ltd.).

[0078]

Example 1

25 The polymerization and stoppage of methyl methacrylate

were carried out by using the continuous bulk polymerization apparatus shown in Fig. 1.

A reaction vessel 10 was a fully mixing reaction vessel (internal volume: 12 L) equipped with a MIG blade as the stirring blade 11 and a jacket 15 covering almost the whole of the reaction vessel.

[0079]

As the raw material monomer fed by a monomer feed means, a mixture (A) containing 92.97% by weight of methyl methacrylate (MMA), 6.90% by weight of methyl acrylate (MA) and 0.13% by weight of a chain transfer agent (n-octyl mercaptan) was used. A feed flow rate of the monomer at the start of the polymerization was fixed at 17.55 kg/hr by a monomer feed pump 20. A stirring motive energy was 24.8 kW.

The temperature T2 (degrees Celsius) of an external wall of the reaction vessel 10 was controlled at 140 degrees Celsius using the temperature adjustment and control means 33.

[0080]

Further, as a polymerization initiator and the like fed by the polymerization initiator feed means, a mixture (B)

containing 92.83% by weight of methyl methacrylate (MMA),
6.90% by weight of methyl acrylate (MA), 0.13% by weight of
a chain transfer agent (n-octylmercatan) and 0.14% by weight
of a polymerization initiator (t-amyl peroxy-2-ethyl-
5 hexanoate) was used. A triple-barreled reciprocal pump was
used for the initiator feed pump 25. Further, its feed flow
rate was set at 1.03 kg/hr at the start of polymerization
and then, suitably fluctuated by changing the output value
of the pump so that the temperature T1 (degrees Celsius) in
10 the reaction vessel 10 was kept at 140 degrees Celsius.

[0081]

The polymerization was continuously carried out for
about 1 day. During this polymerization, the temperature T1
15 (degrees Celsius) in the reaction vessel 10 was in a range
of about 139.6 to 140.4 degrees Celsius.

[0082]

Then, the polymerization was stopped as follows for
20 inspection of apparatus at the downstream side. As the raw
material monomer fed by a monomer feed means, a mixture (C)
containing 92.97% by weight of methyl methacrylate (MMA),
6.90% by weight of methyl acrylate (MA) and 0.13% by weight
of a chain transfer agent (n-octyl mercaptan) was used.

[0083]

The monomer feed pump 20 and the initiator feed pump 25 were controlled to stop the supply of the raw material monomer, the polymerization initiator and the like. Subsequently, the valve of the junction of the initiator feed line (piping) 28 and the monomer feed line (piping) 58 is changed to connect the initiator feed pump 25 with the monomer feed tank 56 through the monomer feed line (piping) 58, and the initiator feed pump 25 was controlled to supply the mixture (C) into the reaction vessel 10 at the flow rate of 0.35 kg/hr through the monomer feed line (piping) 58 from the monomer feed tank 56. During the polymerization stoppage, the mixture (C) was supplied by supplying and babbling the nitrogen gas into the mixture (C) in the monomer feed tank 56 from the inactive gas introduction line 56a, and the dissolved oxygen concentration of the mixture (C) supplied into the reaction vessel 10 was changed between 0 ppm and 1 ppm.

[0084]

The polymerization was stopped for about three days, and the temperature T1 (degrees Celsius) in the reaction vessel 10 was in a range of about 140 to 145 degrees Celsius during the period of this stoppage. The temperature T2 (degrees Celsius) of an external wall of the reaction vessel

10 was controlled at 140 degrees Celsius in the manner as at the polymerization.

[0085]

5 After polymerization stoppage for about three days, a predetermined amount of the raw material was fed in the same manner as the above, and a mixture of the polymerization initiator was suitably fluctuated and fed by changing the output value of the pump so that the temperature T1 (degrees
10 Celsius) in the reaction vessel 10 was kept at 140 degrees Celsius, to carry out the continuous polymerization. A similar polymer as the polymer before stoppage of the polymerization was obtained without incorporation of gels.

15 [0086]

Example 2

The polymerization was conducted in the same procedure as in Example 1. The polymerization was performed for about one day as in Example 1.

20

For an apparatus check of a downstream side, the polymerization was discontinued as follows.

The monomer feed pump 20 and the initiator feed pump 25
25 were controlled to stop the supply of the raw material

monomer, the polymerization initiator and the like. Subsequently, the valve of the junction of the initiator feed line (piping) 23 and the monomer feed line (piping) 53 is changed to connect the monomer feed pump 20 with the monomer feed tank 51 through the monomer feed line (piping) 53, and the monomer feed pump 20 was controlled to supply the mixture (C) into the reaction vessel 10 at the flow rate of 0.29 kg/hr through the monomer feed line (piping) 53 from the monomer feed tank 51. During the polymerization stoppage, the supply of the mixture (C) from the monomer feed tank 51 was performed by supplying and babbling the nitrogen gas into the mixture (C) in the monomer feed tank 51 from the inactive gas introduction line 51a, and the dissolved oxygen concentration of the mixture (C) supplied into the reaction vessel 10 was changed between 0 ppm and 1 ppm. On the hand, the valve of the junction of the initiator feed line (piping) 28 and the monomer feed line (piping) 58 was changed to connect the initiator feed pump 25 with the monomer feed tank 56 through the monomer feed line (piping) 58. The initiator feed pump 25 was controlled to supply the mixture (C) into the reaction vessel 10 at the flow rate of 0.06 kg/hr from the monomer feed tank 56 through the monomer feed line (piping) 58. The dissolved oxygen concentration of the mixture (C) supplied into the reaction vessel 10 from the monomer feed tank 56 was changed

between 10 ppm and 14 ppm. The total flow rate of the raw material supplied into the reaction vessel 10 from the monomer feed tanks 51 and 56 was 0.35 kg/hr, and the dissolved oxygen concentration in the raw material was 3 to 4 ppm.

[0087]

The polymerization was stopped for about three days, and the temperature T1 (degrees Celsius) in the reaction vessel was in a range of about 140 to 145 degrees Celsius during the period of this stoppage. The temperature T2 (degrees Celsius) of an external wall of the reaction vessel 10 was controlled at 140 degrees Celsius in the manner as at the polymerization.

[0088]

Comparative Example 1

The same procedure was repeated as in Example 2 except that the supply of the mixture (C) from the monomer feed tank 51 during polymerization stoppage without babbling the nitrogen gas in the mixture (C) in the monomer feed tank 51.

The total flow rate of the raw material supplied into the reaction vessel 10 from the monomer feed tanks 51 and 56 was 0.35 kg/hr, and the dissolved oxygen concentration in

the raw material was 10 to 14 ppm. The polymerization was stopped so that the temperature T2 of the outer wall side of the reaction vessel 10 (degrees Celsius) was controlled at 140 (degrees Celsius) as in the time of polymerization, but
5 the temperature T1 in the reaction vessel 10 (degrees Celsius) continued rising from 140 degrees Celsius to about 200 degrees Celsius over about 40 hours from the stoppage start.

10 [0089]

Comparative example 2

The polymerization was performed in the same manner as in Example 1. The Polymerization was performed for about one day as in Example 1.

15

For an apparatus check of a downstream side, the polymerization was discontinued as follows.

The monomer feed pump 20 and the initiator feed pump 25
20 were controlled to stop the supply of the raw material monomer, the polymerization initiator and the like. Subsequently, the valve of the junction of the monomer feed line (piping) 23 and the monomer feed line (piping) 53 is changed to connect the monomer feed pump 20 with the monomer
25 feed tank 51 through the monomer feed line (piping) 53, and

the monomer feed pump 20 was controlled to supply the mixture (C) into the reaction vessel 10 at the flow rate of 0.29 kg/hr through the monomer feed line (piping) 53 from the monomer feed tank 51. The dissolved oxygen concentration of the mixture (C) supplied into the reaction vessel 10 was changed between 6 ppm and 7 ppm. On the hand, the valve of the junction of the initiator feed line (piping) 28 and the monomer feed line (piping) 58 was changed to connect the initiator feed pump 25 with the monomer feed tank 56 through the monomer feed line (piping) 58. The initiator feed pump 25 was controlled to supply the mixture (C) into the reaction vessel 10 at the flow rate of 0.06 kg/hr from the monomer feed tank 56 through the monomer feed line (piping) 58. The dissolved oxygen concentration of the mixture (C) supplied into the reaction vessel 10 from the monomer feed tank 56 was changed between 6 ppm and 7 ppm. The total flow rate of the raw material supplied into the reaction vessel 10 from the monomer feed tanks 51 and 56 was 0.35 kg/hr, and the dissolved oxygen concentration in the raw material was 6 to 7 ppm.

[0090]

The polymerization was stopped so that the temperature T2 of the outer wall side of the reaction vessel 10 (degrees Celsius) was controlled at 140 (degrees Celsius) as in the

time of polymerization, but the temperature T1 in the reaction vessel 10 (degrees Celsius) continued rising from a stop from 140 degrees Celsius to about 200 degrees Celsius over about 40 hours from the stoppage start.

5

INDUSTRIAL AVAILABILITY

[0091]

The method of the present invention can be used for the continuous polymerization (especially continuous bulk polymerization) of various polymers. Examples of the polymer include polymers formed from at least one of monomers selected from the group consisting of a methacrylate ester monomer, an acrylate ester monomer, styrene and acrylonitrile.

15

EXPLANATION OF REFERENCE NUMERALS

[0092]

10	Reaction vessel
11	Stirring blade
20	15 Jacket (Temperature control means)
	20 Monomer feed pump (Monomer feed means)
	21, 51, and 56 Monomer feed tank
	25 Initiator feed pump (Initiator feed means)
	26 Initiator feed tank
25	30 Control portion (Feed flow rate control means)

35 Temperature sensor (Temperature detection means)

CLAIMS

1. A method of stopping a continuous polymerization, which comprises continuously supplying a monomer and a
5 polymerization initiator into a reaction vessel to polymerize the monomer in the reaction vessel; and continuously removing a polymerization composition from an inside of the reaction vessel to an outside of the reaction vessel,
10 wherein, the method comprises:
discontinuing the supply of the polymerization initiator into the reaction vessel, and
continuously supplying a monomer-containing raw material having a dissolved oxygen concentration of 0 to 5 ppm into
15 the reaction vessel at a flow rate in a range of 1/500 to 1/10 of a flow rate of a raw material supplied at the polymerization reaction,
in the state that the stirring in the reaction vessel and the removal of a polymerization composition to the outside
20 out of the reaction vessel are continued.
2. The method of stopping continuous polymerization according to claim 1, wherein the monomer contains at least 50 % by weight of methyl methacrylate.

3. The method of stopping continuous polymerization according to claim 1 or 2, wherein the continuous polymerization is a continuous bulk polymerization.

5 4. The method of stopping continuous polymerization according any one of claims 1 to 3, wherein a concentration of dissolved oxygen is adjusted by a bubbling of inert gas, a vacuum deaeration, or a supply of insert gas into a line mixer.

10

5. The method of stopping continuous polymerization according to claim 4, wherein the inert gas is at least one selected from the group consisting of a nitrogen gas, a helium gas, a neon gas and an argon gas.

15

6. The method of stopping continuous polymerization according any one of claims 1 to 5, wherein said raw material is a raw material having a dissolved oxygen concentration of 0 to 5 ppm and consisting of the monomer,
20 or a raw material having a dissolved oxygen concentration of 0 to 5 ppm and consisting of the monomer and a chain transfer agent.