

DESCRIPTION

POLYMERIZATION REACTION APPARATUS AND
METHOD OF PRODUCING POLYMER BY USING THE SAME

5

TECHNICAL FIELD

[0001]

The present invention relates to a polymerization reaction apparatus used for producing a polymer and a method of producing the polymer by using the apparatus.

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BACKGROUND OF THE INVENTION

[0002]

The preparation of a polymer such as a (meth)acrylate-based polymer uses a continuous bulk polymerization method or a continuous solution polymerization method wherein a monomer, a polymerization initiator and the like are continuously introduced into a polymerization reaction vessel. Among the above, in the continuous bulk polymerization method, the polymerization reaction is performed in a homogenous phase without using a solvent and a dispersant, so that an advantage of a polymer containing little impurities is obtained. However, since a viscosity of a reaction system is very high, it is required to pay attention to removing heat from the reaction system,

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controlling the polymerization temperature and the like.
On the other hand, the continuous solution polymerization
method has advantages that a polymer containing little
impurities is obtained and that the problem associated with
the continuous bulk polymerization method is reduced due to
5 a low viscosity of the reaction system, but has the problem
that the productivity is decreased due to use of solvents.

[0003]

JP 7-126308 A discloses a method for producing the
10 methacrylate-based polymer by using a continuous bulk
polymerization method, which comprises carrying out a
polymerization reaction by using a completely mixing type
reacting vessel under the condition that the reaction
vessel is fully filled with a liquid medium so that the
15 reaction vessel has substantially no gaseous phase.

[Prior Art Document]

[0004]

[Patent document 1] JP 7-126308 A

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SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

In the polymerization reaction apparatus used for the
25 production of such polymer, a stirring blade fixed to a

shaft is located inside of the polymerization reaction vessel, thereby a raw material mixture containing the monomer and the polymerization initiator is stirred and the polymerization reaction is performed. One end of the shaft
5 is attached to a drive unit, thereby a rotational driving force is transmitted from the drive unit to the shaft so that the shaft and a stirring blade are rotated. The shaft is supported by a shaft seal bearing part arranged between the drive unit and the polymerization reaction vessel. In
10 this shaft seal bearing part, there is provided a shaft seal portion around the shaft so that the reaction mixture in the polymerization reaction vessel does not reach the drive unit.

[0006]

15 However, when a polymerization reaction is continuously performed by using the polymerization reaction apparatus mentioned above, the monomer and the produced polymer in the reaction mixture tend to adhere to a circumference of the shaft seal bearing part, which causes
20 the problem that it is difficult to perform the polymerization reaction due to insufficient rotations of the shaft and the stirring blade.

[0007]

The present invention has been made in light of the
25 aforementioned problems of the prior art. Objects of the

present invention are to provide a polymerization reaction apparatus which can prevent the monomer and the produced polymer in a reaction mixture from adhering to a shaft seal bearing part during the operation and also to provide a method of producing the polymer by using the polymerization reaction apparatus.

MEANS FOR SOLVING THE PROBLEMS

[0008]

10 In order to achieve the objects stated above, the present invention provides a polymerization reaction apparatus comprising:

 a polymerization reaction vessel for performing a polymerization reaction of a raw material mixture

15 comprising a monomer;

 a rotatable shaft;

 a stirring blade fixed to the rotatable shaft, which stirs the raw material mixture within the polymerization reaction vessel; and

20 a shaft seal bearing part which supports the shaft, wherein the shaft seal bearing part comprises a shaft sealing part comprising:

 a shaft seal portion (A);

 a void portion formed between the shaft seal portion (A)

25 and the polymerization reaction vessel;

a shaft seal portion (B) formed between the void portion and the polymerization reaction vessel; and

a liquid inlet for introducing a liquid containing a polymerization inhibitor into the void portion, and

5 wherein the liquid introduced from the liquid inlet is removed through the void portion into the polymerization reaction vessel.

[0009]

10 In the conventional polymerization reaction apparatuses, when the polymerization reaction is performed continuously for a long period of time, the monomer and the polymer produced therefrom in the reaction mixture tend to adhere to the vicinity of the shaft seal bearing part in the polymerization reaction apparatus, thereby causing the

15 problem that the rotations of the shaft and the stirring blade are inferior. Such problem was particularly remarkably caused in the case that the polymerization reaction is performed in such a condition that the shaft seal bearing part contacts with the reaction mixture in the

20 polymerization reaction vessel when the polymerization reaction vessel has a gaseous phase, and in the case that the polymerization reaction is performed in such a condition that the reaction vessel is fully filled with the liquid medium so that the polymerization reaction vessel

25 has substantially no gaseous phase, since the reaction

mixture easily reaches the shaft seal bearing part. In the polymerization reaction apparatus of the present invention, a liquid inlet for introducing a liquid is provided at the void portion between the shaft seal portion (A) in the shaft seal bearing part and the polymerization reaction vessel so that the introduced liquid is removed from a gap between an inside wall of the shaft seal bearing part and the shaft into the polymerization reaction vessel. Therefore, a liquid flow is generated from the shaft seal bearing part to the polymerization reaction vessel, and thus it is difficult for the monomer in the reaction mixture to reach the vicinity of the shaft seal bearing part. In addition, since the liquid introduced into the polymerization reaction vessel contains a polymerization inhibitor, the polymerization reaction of the monomer near the shaft seal bearing part is also inhibited. Furthermore, the provision of the shaft seal portion (B) suppresses a reverse flow of the reaction mixture in the polymerization reaction vessel, which flow reaches the shaft seal bearing part. Since the shaft seal bearing part has a shaft sealing part comprising the shaft seal portion (A), the void portion, the liquid inlet and the shaft seal portion (B), and is arranged so that the liquid introduced from the liquid inlet is then removed through the void portion into the polymerization reaction vessel, the adhesion of the

monomer and the resultant polymer to the vicinity of the shaft seal bearing part is sufficiently suppressed. In addition, the inferior rotations of the shaft and the stirring blade are sufficiently suppressed even when the operation of the apparatus is continued for a long period of time.

[0010]

In the polymerization reaction apparatus of the present invention, the shaft seal portion (A) is preferably formed by a mechanical seal. The mechanical seal can give no deterioration of the shaft seal portion (A) even under a high temperature and a stable continuous operation for a long period of time.

[0011]

In the polymerization reaction apparatus of the present invention, the shaft seal portion (B) is preferably formed by a lip seal. The lip seal can prevent a reverse flow of the reaction mixture from the polymerization reaction vessel into the shaft seal bearing part.

[0012]

The present invention also provides a method of producing a polymer by using the above-mentioned polymerization reaction apparatus, comprising step of: continuously feeding the raw material mixture containing the monomer into the polymerization reaction vessel to

carry out the polymerization reaction, while the liquid containing the polymerization inhibitor is introduced into the void portion through the liquid inlet.

[0013]

5 According to the above-mentioned method of producing the polymer, the polymer can be continuously produced for a long period of time without causing the problems such as the inferior rotations of the shaft and the stirring blade, by carrying out the polymerization method using the above
10 polymerization reaction apparatus with introducing the liquid containing the polymerization inhibitor through the liquid inlet. In addition, the adhesion of the monomer and the polymer produced therefrom to the vicinity of the shaft seal bearing part is sufficiently inhibited.

15 [0014]

 Moreover, with regard to the present method of producing the polymer, the liquid introduced from the liquid inlet is preferably a liquid comprising the monomer in which the polymerization inhibitor is dissolved. In
20 such liquid, the monomer containing the same components as in the monomer contained in the raw material mixture is preferably used as the solvent for dissolving the polymerization inhibitor. Therefore, it is capable of preventing impurities from being mixed into the produced
25 polymer in comparison with the case that another solvent is

used.

EFFECTS OF THE INVENTION

[0015]

5 According to the present invention, the monomer and the resultant polymer in the reaction mixture can be prevented from adhering to the shaft seal bearing part during the operation, the continuous operation for a long period of time can be made without causing the problems of
10 the rotation failures of the shaft and the stirring blade, thus providing the polymerization reaction apparatus continuously operatable for a long period of time and a method of producing a polymer by using the above apparatus.

15 BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 is a schematic structural diagram of a preferable embodiment of a polymerization reaction apparatus according to the present invention.

20 Fig. 2 is a partial cross-sectional view of a shaft seal bearing part of the polymerization reaction apparatus according to the present invention.

EXPLANATION OF REFERENCE NUMERALS

25 10: Polymerization reaction vessel,

- 12: Raw material feeding port,
14: Polymer composition discharge port,
16: Jacket,
20: Shaft,
5 22: Stirring blade,
30: Shaft seal bearing part,
32: Shaft seal portion (A),
34: Void portion,
36: Liquid inlet,
10 38: Shaft seal portion (B),
40: Shaft sealing part,
100: Polymerization reaction apparatus,
101: Initiator preparation vessel,
102: Monomer preparation vessel.

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EXPLANATION OF EMBODIMENTS

[0017]

Hereafter, preferred embodiments of the present invention will be described in detail with reference to the drawings. In each of the drawings, the same or the
20 corresponding element is denoted with the same number, for which redundant description may be omitted. Moreover, dimensional ratios are not limited to the dimensional ratios shown in the drawings.

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[0018]

Fig. 1 is a schematic structural diagram of a preferable embodiment of a polymerization reaction apparatus according to the present invention. As shown in Fig. 1, the polymerization reaction apparatus 100 is equipped with a polymerization reaction vessel 10 in which the polymerization reaction of the raw material mixture containing the monomer is performed, a rotatable shaft 20, a stirring blade 22 which is fixed to the rotatable shaft 20, which stirs the raw material mixture within the polymerization reaction vessel 10, and a shaft seal bearing part 30 which supports the shaft 20. Moreover, the polymerization reaction apparatus 100 is equipped with a raw material feeding port 12 for feeding the raw material to the polymerization reaction vessel 10 and a polymer composition discharge port 14 for discharging, out of the polymerization reaction vessel 10, a liquid (syrupy) polymer composition containing the polymer produced by the polymerization reaction. Furthermore, the polymerization reaction apparatus 100 is equipped with a jacket 16 for adjusting a temperature of an external wall of the polymerization reaction vessel 10.

[0019]

Fig. 2 is a partial cross-sectional view of a shaft seal bearing part of the polymerization reaction apparatus according to the present invention. As shown in Fig. 2,

the shaft seal bearing part 30 has a shaft sealing part 40 comprising a shaft seal portion (A) 32; a void portion 34 which is formed between the shaft seal portion (A) 32 and the polymerization reaction vessel 10; a shaft seal portion (B) 38 which is formed between the void portion 34 and the polymerization reaction vessel 10; and a liquid inlet 36 for introducing a liquid containing a polymerization inhibitor into the void portion 34. The shaft seal bearing part 30 has a bearing which supports the shaft 20 in addition to the shaft sealing part 40. The liquid containing the polymerization inhibitor which is introduced in the void portion 34 is removed into the polymerization reaction vessel 10 through the void portion 34. In this embodiment, the shaft seal portion (B) 38 is located between the void portion 34 and the polymerization reaction vessel 10. As the shaft seal portion (B) 38, a lip seal, a PTFE (polytetrafluoroethylene) bush and the like may be used, and the lip seal is preferable. The shaft seal portion (B) 38 is preferably made from PTFE. Use of the shaft seal portion (B) 38 made from PTFE contributes to increase chemical resistance to monomer and suitably maintains good sealing property even if a vibration of the shaft occurs. Thus, even when the apparatus is continuously operated for a long period of time, good sealing effect can be sustained. Moreover, there is

provided a drive unit (not shown) for rotationally driving the shaft 20 above the shaft seal portion (A) 32 (which is in the direction opposite to the polymerization reaction vessel 10).

5 [0020]

The shaft seal portion (A) 32 may be formed in any forms of well known shaft seal, however it preferably has a mechanical seal as shown in Fig. 2, because it scarcely causes problems such as the seal failure due to the liquid
10 introduced in the void portion 34. Since the type of the mechanical seal is not particularly limited, any types of mechanical seal may be selected from those which are well known to the skilled person. For example, as shown in Fig. 2, the mechanical seal has a rotary ring 32a which is fixed
15 on a side of the shaft 20 and a stationary ring 32b which is fixed on a side of a main body (a casing) of the shaft seal bearing part and is constructed so that the rotary ring 32a and the stationary ring 32b are pressed against each other at a constant pressure exerted by a spring (not
20 shown). In addition, in order to reduce a friction between the contact surfaces of the rotary ring 32a and the stationary ring 32b, an inside of the mechanical seal is filled up with a mechanical seal liquid 32c. In Fig. 2, there is shown a construction of a pair of mechanical seals
25 each having the combination of the rotary ring 32a and the

stationary ring 32b, that is, a construction of a double mechanical seal. The mechanical seal liquid 32c is generally continuously fed through an inlet for the mechanical seal liquid (not shown) by a pump and the like, and continuously discharged through an outlet for the mechanical seal liquid (not shown). It is preferable that the mechanical seal liquid is circularly supplied. A filling pressure is suitably set depending on the size of the polymerization reaction apparatus 100 and the polymerization conditions and the like and is set higher than the pressure of the liquid introduced into the void portion 34.

[0021]

As the mechanical seal liquid 32c, any of the well-known mechanical seal liquids can be used particularly without limitation. Specifically, for example, adipate esters, phthalate esters, diisobutyrate esters and acetylated glycerides may be used. The adipate esters include, for example, bis(2-ethylhexyl) adipate, diisononyl adipate and diisodecyl adipate. The phthalic esters include, for example, bis(2-ethylhexyl) phthalate, diisononyl phthalate and diisodecyl phthalate. The diisobutyrate esters include, for example, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. The acetylated glycerides include, for example, glycerol diacetomonomonolaurate, glycerol

diacetomonostearate, glycerol diacetomonooleate, glycerol diacetomonolinolate, glycerol diacetomono-12-hydroxystearate, glycerol diacetomonomyristate, glycerol diacetomonopalmitate, glycerol diacetomonolaurate, glycerol monoacetomonostearate, glycerol monoacetomonomyristate, glycerol monoacetomonopalmitate, glycerol monoacetomonoricinolate, glycerol monoacetomono-12-hydroxystearate, glycerol monoacetomonobehenate, glycerol monoacetomonooleate, glycerol monoacetomonolaurate, glycerol monoacetodioleate, glycerol monoacetodiricinolate, glycerol monoacetodicaprylate, and glycerol monoacetodilaurate, glycerol monoacetodistearate. Among them, adipate esters and diisobutyrate esters are preferable and adipate eaters are particularly preferable.

When a (meth)acrylate-based polymer, particularly polymethyl methacrylate (PMMA) is produced as the polymer, adipate esters have the advantages that they do not facilitate the polymerization reaction of the monomer and that they scarcely cause adverse affects such as coloration of the resultant polymer, even if they are mixed with the reaction mixture.

[0022]

The materials for the rotary ring 32a and the stationary ring 32b are not particularly limited, and any well known material can be used. The material for the

rotary ring 32a and the stationary ring 32b includes, for example, carbon, silicon carbide, cemented carbide, and chrome oxide coating.

[0023]

5 The shaft seal portion (A) 32 can also be formed by, for example, a gland packing, a Wilson seal, an oil seal, a labyrinth seal, an O-ring seal and a bellows seal in addition to the mechanical seal.

[0024]

10 The liquid to be introduced into the void portion 34 through the liquid inlet 36 is a liquid containing a polymerization inhibitor, and it is preferable that the liquid comprises a solvent which does not promote the polymerization reaction of the monomer in the reaction
15 mixture, into which the polymerization inhibitor was dissolved. The above solvent includes, for example, an organic solvent such as toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, octane, decane, cyclohexane, decalin, butyl acetate, and
20 pentyl acetate, and a monomer which is the same as the monomer contained in the raw material mixture. The monomer which is the same as the monomer contained in the raw material mixture is particularly preferable. The above monomer is typically a liquid. When the above monomer is
25 used as the solvent, it is capable of preventing impurities

from being mixed into the produced polymer. Since the above liquid contains the polymerization inhibitor, the polymerization reaction of the monomer which is the solvent can be suppressed also in the above liquid.

5 [0025]

The polymerization inhibitor includes, for example, hydroquinone, hydroquinone monomethyl ether, tert-butylcatechol, 4-methoxy-1-naphthol, 1,4-naphthoquinone, 2,4-dimethyl-6-tert-butyl phenol, phenothiazine, 10 benzophenothiazine, dinitrobenzene, p-phenyldiamine and dimethyldithiocarbamate salt. Among these, 2,4-dimethyl-6-tert-butyl phenol is preferable from the view point that it scarcely causes adverse affects such as coloration of the obtained polymer when it remains in the polymer. The 15 polymerization inhibitor to be used is suitably selected depending on the polymer to be produced and the monomer to be used as the raw material.

[0026]

Preferably, the content of polymerization inhibitor in 20 the above liquid is in the range from 5 to 2,000 ppm by mass on the basis of the whole quantity of the liquid, more preferably in the range from 10 to 500 ppm by mass. The content of the above mentioned range can give no coloration of the polymer and good polymerization reaction of the raw 25 material monomer at the vicinity of the shaft seal bearing

part 30 even if the monomer is used as the solvent.

[0027]

The flow rate of the liquid to be introduced is suitably set depending on the size of the polymerization reaction apparatus 100, the polymerization conditions and the like, which is typically in the range from 0.01 to 5 L/min, and preferably in the range from 0.1 to 3 L/min. The flow rate of the liquid in the above range can give no coloration of the polymer, and good prevention of the unreacted monomer and the polymer contained in the reaction mixture from entering into the shaft seal bearing part 30. The polymerization reaction of the raw material mixture within the polymer reaction vessel 10 is performed while continuously supplying the liquid from the liquid inlet 36 into the void portion 34 at the above-mentioned flow rate.

[0028]

In the polymerization reaction apparatus 100, the void portion 34 is equipped with the liquid inlet 36, and the introduction of the liquid through the liquid inlet gives a pressurized state of the inside of the void portion 34, thereby generates higher pressure than the inside of the polymerization reaction vessel 10. Then, it is capable of sufficiently preventing the reaction mixture from entering into the shaft seal bearing part 30 from the polymerization reaction vessel 10 and functions as the shaft seal. In the

meanwhile, although the suitable range of the pressure in the void portion 34 is suitably set depending on the size of the polymerization reaction apparatus 100 and the polymerization conditions and the like, it is preferably set higher than the pressure in the polymerization reaction vessel 10 and lower than the filling pressure of the mechanical seal liquid 32c. Preferably, a safety device such as a relief valve is provided at a body of a pump for transferring the liquid so as to avoid the pressure from increasing excessively. In addition, since a pressure gauge and a safety valve are provided in the polymerization reaction apparatus 100, the pressure in the void portion 34 is set in a range in which the safety valve does not operate. The shaft seal bearing part 30 is located at an uppermost part of the reaction vessel 10 in Fig. 1, but it may be located at a lower part of the reaction vessel 10. Even when the shaft seal bearing part is located at the position where the shaft seal bearing part contacts with the reaction mixture in the polymerization reaction vessel during performing the polymerization reaction in the condition that gaseous phase is present in the polymerization reaction vessel; or when the shaft seal bearing part is located at the position where the shaft seal bearing part contacts with the reaction mixture in the polymerization reaction vessel during performing the

polymerization reaction in the liquid-full condition that gaseous phase is substantially absent in the polymerization reaction vessel, it is capable of sufficiently preventing the reaction mixture from entering into the shaft seal bearing part 30 from the polymerization reaction vessel 10, because the polymerization reaction apparatus 100 has the shaft seal bearing part 30 having the above construction.

[0029]

The polymerization reaction apparatus 100 of this embodiment is a continuous polymerizing apparatus, which is used for a continuous bulk polymerization method or a continuous solution polymerization method, wherein the polymerization reaction vessel 10 can form substantially complete mixing state within the reaction vessel by the stirring blade 22. A shape of the stirring blade 22 may be Max blend wings (manufactured by Sumitomo Heavy Industries, Ltd.), paddle wings, double helical ribbon wings, MIG wings, full zone wings (manufactured by Shinko Pantec Co., Ltd.) and the like, but it is not particularly limited thereto. In addition, it is preferable to install one or more baffles in the polymerization reaction vessel 10 in order to improve the stirring effect.

[0030]

The higher stirring effect is preferable with regard to the polymerization reaction apparatus 100. However, the

application of an excessive stirring power is not so preferable, since excess heat quantity is provided. Therefore, the stirring power is preferably in the range from 0.5 to 20 kW/m³, more preferably in the range from 1 to 15 kW/m³. It is preferable to increase the stirring power, as the viscosity of the content liquid, that is, the content ratio of the polymer in the liquid increases.

[0031]

Preferably, the inside of the polymerization reaction vessel 10 is in the liquid-full condition that a gaseous phase is substantially absent. The liquid-full condition of the polymerization reaction vessel prevents the polymer from forming at or from adhering to the inside wall of the vessel on the gaseous phase and the gas-liquid interface, so that the possible quantity degradation of the product caused by mixing of the polymer prepared at the inside wall may be avoided. In addition, the whole volume of the polymerization reaction vessel 10 can be effectively used, so that the productivity can be improved.

[0032]

In order to put the polymerization reaction vessel 10 into the liquid-full condition, it is the simplest way to locate an outlet for the polymer composition after the polymerization reaction (a polymer composition discharge port 14) at the uppermost part of the reaction vessel 10 as

shown in Fig. 1. In this case, it is preferable that a supply port 12 for the raw material (an initiator compositions and a monomer compositions) is located at the lower part of the polymerization reaction vessel 10 as shown in Fig. 1. In addition, it is desirable to prevent a gas of the raw material monomer from generating in the polymerization reaction vessel 10. To this end, it is preferable to make the pressure in the polymerization reaction vessel 10 to exceed a vapor pressure of the reaction mixture at the temperature of the reaction vessel 10. This pressure is generally in the range from about 1.0 to about 2.0 MPa in terms of a gage pressure.

[0033]

Moreover, it is preferable to make the inside of the polymerization reaction vessel 10 to be an adiabatic state that heat cannot substantially enter from and exit into outside of the vessel. That is, it is preferable to make the temperature in the reaction vessel and the temperature of the external wall surface of the reaction vessel to be almost the same temperature. Specifically, said same temperature can be achieved by providing a jacket 16 at the external wall surface of the reaction vessel, thereby controlling the temperature of the external wall surface thereof so as to follow the internal temperature of the reaction vessel using a heat medium such as steam or other

heat medium, for example, as shown in Fig. 1.

[0034]

The jacket 16 covers substantially a whole external surface of the polymerization reaction vessel 10 and can properly heat or keep the temperature of the reaction vessel 10 by introducing a heat medium such as steam, hot water and an organic heating medium into the jacket 16 through a heat medium supply path (not shown). The temperature of the jacket 16 can be suitably adjusted by the temperature or the pressure of the supplied heat medium. The heat medium introduced into the jacket 16 is discharged through a heat medium discharge path (not shown).

[0035]

The provision of the adiabatic state of the reaction vessel 10 is to prevent the polymer from adhering to the inside wall in the reaction vessel and to stabilize the polymerization reaction, thereby giving a self-controlled property for suppressing a possible runaway reaction. The setting of the internal temperature of the reaction vessel to a temperature which is too higher than that of the content liquid is not preferable, since an excess heat is added to the inside of the reaction vessel. Preferably, a temperature difference between the reaction vessel and the external wall surface of the reaction vessel is as small as possible and the temperature difference may be practically

adjusted within the degree of instability of the range $\pm 5^{\circ}\text{C}$.

[0036]

In this embodiment, the heat generated within the polymerization reaction vessel 10, that is, the heat of polymerization and the heat of stirring are preferably balanced with the quantity of heat taken away by the (syrupe) liquid polymer composition discharged from the polymerization reaction vessel 10. The quantity of heat taken away by the polymer composition is determined by the amount of the polymer composition, the specific heats and the temperatures (polymerization temperature).

[0037]

The polymerization temperature is preferably in the range from about 120 to 180°C , more preferably in the range from about 130°C to about 180°C depending on the type of radical polymerization initiator used. When the polymerization temperature is too high, there is the tendency that the syndiotacticity of the obtained polymer becomes low, the amount of generated oligomer increases, and the heat resistance of a resultant resin becomes low.

[0038]

The mean residence time of the raw material mixture within the polymerization reaction vessel 10 is preferably in the range from 15 minutes to 2 hours, more preferably in the range from 20 minutes to 1.5 hours. When the residence

time is longer than required, there arises a tendency that the production of oligomer such as dimers and trimers increases so that a heat-resistance property of the product decreases. The mean residence time can be adjusted by changing a supply amount of the monomer per unit time.

[0039]

Supply of the raw material into the polymerization reaction vessel 10 may be performed by feeding the polymerization initiator composition containing the radical polymerization initiator from an initiator supply conduit 51 and the monomer composition containing the monomer from a monomer supply conduit 52, separately from the feeding port 12;

by feeding the mixture of the initiator composition and the monomer composition from the feeding port 12 by merging the initiator supply conduit 51 between an initiator supply pump 53 and the feeding port 12 with the monomer supply conduit 52 between a monomer supply pump 54 and the feeding port 12; or

by feeding each of the initiator composition and the monomer composition from each corresponding feeding port by forming a feeding port different from the feeding port 12 (not shown). The initiator composition contains, for example, a mixture of a radical polymerization initiator, a monomer and a chain transfer agent, and the monomer

composition contains, for example, a mixture of a monomer and a chain transfer agent.

[0040]

5 The initiator composition is prepared in the initiator preparation vessel 101. The prepared initiator composition is continuously supplied to the polymerization reaction vessel 10 by the initiator supply pump 53 through the initiator supply conduit 51 which connects the initiator preparation vessel 101 with the polymerization reaction vessel 10, as shown in Fig. 1. On the other hand, the monomer composition is prepared in the monomer preparation vessel 102. The prepared monomer composition is continuously supplied to the polymerization reaction vessel 10 by the monomer supply pump 54 through the monomer supply conduit 52 which connects the monomer preparation vessel 102 with the polymerization reaction vessel 10 as shown in Fig. 1.

[0041]

20 As the initiator preparation vessel 101 and the monomer preparation vessel 102 which are used in this embodiment, a preparation vessel equipped with a stirring device which is similar to the polymerization reaction vessel 10 may be used. In the initiator preparation vessel 101, a radical polymerization initiator is thoroughly dissolved in the monomer to give an initiator liquid. The

25

temperature in the initiator preparation vessel 101 is maintained at a temperature at which the polymerization reaction does not proceed, preferably maintained at -20°C to 10°C. On the other hand, the temperature in the monomer preparation vessel 102 is maintained at a temperature at which the monomer does not volatilize, preferably maintained at -20°C to 10°C.

[0042]

The initiator supply pump 53 and the monomer supply pump 54 are not particularly limited, and are preferably a pump which can set the supply flow rates of the initiator composition and the monomer composition to the polymerization reaction vessel 10 at a constant rate. Specifically, it is preferable to use a multiple reciprocating pump, more preferably a nonpulsatile controlled-volume type pump such as a twin nonpulsatile controlled-volume type pump and a triple nonpulsatile controlled-volume type pump.

[0043]

Heating/cooling devices may be connected with the initiator supply conduit 51 and the monomer supply conduit 52, which connect the initiator preparation vessel 101 and the monomer preparation vessel 102 with the polymerization reaction vessel 10, thereby adjusting the temperature of the raw material which is fed to the polymerization

reaction vessel 10.

[0044]

The supply rate of the initiator composition from the initiator preparation vessel 101 to the polymerization reaction vessel 10, which varies depending on the capacity of the polymerization reaction vessel 10, is preferably in the range from 0.1 to 10 kg/hr, more preferably in the range from 0.5 to 5 kg/hr, in the case that the capacity of the polymerization reaction vessel 10 is 10 L. The supply rate of the monomer composition from the monomer preparation vessel 102 to the polymerization reaction vessel 10, which varies depending on the capacity of the polymerization reaction vessel 10, is preferably in the range from 4 to 40 kg/hr, more preferably in the range from 10 to 30 kg/hr in the case that the capacity of the polymerization reaction vessel 10 is 10 L.

[0045]

In order to avoid the influence due to dissolved oxygen during the preparation of the monomer, it is common to carry out bubbling of an inert gas into the monomer preparation vessel 102 or to deaerate under reduced pressure to remove dissolved oxygen. In this embodiment, it is not necessary to strictly remove the dissolved oxygen and the polymerization reaction can be performed in the presence of the dissolved oxygen in about 1.5 ppm to 3 ppm.

In the case that the obtained polymer is used for the material of optical apparatus, it is particularly desirable to filtrate the monomer composition with a filter having pores corresponding to a desired size in order to remove
5 impurities during feeding the prepared monomer composition to the polymerization reaction vessel 10.

[0046]

The polymer produced by the polymerization reaction using the polymerization reaction apparatus 100 is removed
10 through the polymer composition discharge port 14 of the polymerization reaction vessel 10 as a (syropy) liquid polymer composition, transferred via a polymer composition lead-out passage 55 and recovered. Since the polymer composition contains unreacted raw material monomer,
15 volatile substances mainly containing the unreacted raw material monomer are separated by evaporation by heating the polymer composition as necessary. As the transfer procedure of the above polymer composition, the procedure disclosed in JP 4-48802 B is suitable. As the procedure
20 for the separation by evaporation of the volatile matters, the procedures using a vented extruder is known, for example, the procedures disclosed in JP 51-29914 B, JP 52-17555 B, JP 1-53682 B, JP 62-89710 A and JP 3-49925 A are suitable.

25 [0047]

The polymerization reaction vessel 10 used for the present invention is preferably a completely mixing type reacting vessel, a polymerization (conversion) rate of the raw monomer to the polymer within the reaction vessel generally corresponds to the content ratio of the polymer in the polymer composition. In the present invention, although the rate of polymerization is not particularly limited, it is usually set in the range from 40 to 70% by mass. As the rate of polymerization becomes higher, the productivity of the polymer increases, but higher viscosity of the reaction system is resulted to require a large extent of stirring power. As the rate of polymerization becomes lower, the productivity of the polymer decreases so that the burden for recovering the unreacted raw material monomer is increased.

[0048]

The unreacted raw material monomer which is separated and collected from the polymer composition are stored in a monomer recovery tank and may be supplied to the polymerization reaction by feeding to the monomer preparation vessel 102 as necessary. It is preferable to store the recovered raw monomer under the condition that a the concentration of the polymerization inhibitor is from 2 ppm to 8 ppm and the concentration of oxygen in the gaseous phase is from 2% to 8% by volume so as not to proceed the

polymerization reaction during storing in the monomer recovery tank. It is preferable to store in a cooled condition, specifically, at a temperature, for example, around from about 0°C to about 5°C.

5 [0049]

With regard to the present invention, although the monomer, the radical polymerization initiator and the chain transfer agent are selected depending on the polymer to be produced, the raw materials will be explained hereinafter
10 in the case that (meth)acrylate polymer such as polymethyl methacrylate is produced as preferable embodiments. In the present specification, the term "(meth)acryl" means an "acryl" group and a "methacryl" group.

[0050]

15 The monomer to be used as the raw material for the (meth)acrylate polymer is not particularly limited, and includes, for example, an alkyl (meth)acrylate alone (wherein the alkyl group has 1 to 4 carbon atoms), or a mixture of at least 80% by weight of alkyl (meth)acrylate
20 (wherein the alkyl group has 1 to 4 carbon atoms) and at most 20% by weight of another vinyl monomer copolymerizable therewith. The alkyl group in the alkyl (meth)acrylate (wherein the alkyl group has 1 to 4 carbon atoms) includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl
25 and t-butyl. Methyl (meth)acrylate is preferable among the

alkyl (meth)acrylates.

[0051]

The copolymerizable vinyl monomer mentioned above includes, for example, a (meth)acrylate ester other than
5 the above alkyl (meth)acrylate (wherein the alkyl group has 1 to 4 carbon atoms), such as benzyl (meth)acrylate and 2-ethylhexyl (meth)acrylate; an unsaturated carboxylic acid or anhydride thereof such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride and itaconic
10 acid anhydride; a monomer containing a hydroxyl group such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglycerol acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and monoglycerol methacrylate; a monomer containing nitrogen, such as acrylamide,
15 methacrylamide, acrylonitrile, methacrylonitrile, diacetone acrylamide and dimethylaminoethyl methacrylate; a monomer containing an epoxy group such as allyl glycidyl ether, glycidyl acrylate and glycidyl methacrylate; and a styrene monomer such as styrene and alpha-methylstyrene.

20 [0052]

When the present invention is applied to the production of a polymer based on (meth)acrylate ester, the polymerization initiator supplied to the reaction vessel includes, for example, a radical polymerization initiator.
25 The radical polymerization initiator includes, for example,

azo compounds such as azobisisobutyronitrile,
 azobisdimethylvaleronitrile, azobiscyclohexanenitrile,
 1,1'-azobis-(1-acetoxy-1-phenylethane), dimethyl 2,2'-
 azobisisobutyrate, 4,4'-azobis-4-cyanovaleric acid; organic
 5 peroxides such as benzoyl peroxide, lauroyl peroxide,
 acetyl peroxide, caprylyl peroxide, 2,4-dichloro benzoyl
 peroxide, isobutyl peroxide, acetyl cyclohexyl sulfonyl
 peroxide, t-butyl peroxy-pivalate, t-butyl peroxy
 neodecanoate, t-butyl peroxy neoheptanoate, t-butylperoxy-
 10 2-ethyl hexanoate, 1,1-di(t-butylperoxy)cyclohexane, 1,1-
 di(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(t-
 hexylperoxy)-3,3,5-trimethylcyclohexane, isopropyl
 peroxydicarbonate, isobutyl peroxydicarbonate, s-butyl
 peroxydicarbonate, n-butyl peroxydicarbonate, 2-ethylhexyl
 15 peroxydicarbonate, bis(4-t-butylcyclohexyl)peroxy
 dicarbonate, t-amyl peroxy-2-ethyl hexanoate, 1,1,3,3-
 tetramethylbutyl peroxyethylhexanoate, 1,1,2-
 trimethylpropyl peroxy-2-ethylhexanoate, t-butylperoxy
 isopropyl monocarbonate, t-amyl peroxyisopropyl
 20 monocarbonate, t-butylperoxy-2-ethylhexyl carbonate, t-
 butyl peroxyallyl carbonate, t-butyl peroxy isopropyl
 carbonate, 1,1,3,3-tetramethylbutyl peroxy isopropyl
 monocarbonate, 1,1,2-trimethylpropyl peroxyisopropyl
 monocarbonate, 1,1,3,3-tetramethylbutyl peroxyisononanoate,
 25 1,1,2-trimethylpropylperoxy isononanoate and t-butyl

peroxybenzoate. The above radical polymerization initiator can be used solely or as a mixture of two or more thereof.

[0053]

The amount of the radical polymerization initiator is not particularly limited, and is typically in the range from 0.001 to 1 part by mass based on 100 parts by mass of the raw material monomer. When two or more radical polymerization initiators are used in a mixture, the total amount thereof may be within the above range. The polymerization initiator supplied to the reaction vessel, which is not particularly limited in the present invention, is selected depending on the types of the polymer to be produced and the raw material monomer to be used. For example, the radical polymerization initiator preferably has a half-life of at most 1 minute at the polymerization temperature. When the half-life at the polymerization temperature is at most 1 minute, the reaction rate is suitable, thus the initiator is suitable for the polymerization reaction in the continuous polymerization apparatus. The relationship between the temperature and the half-life of the radical polymerization initiators are described in various articles and the technical documents of manufacturing companies for every type of the radical polymerization initiator. In the present invention, the values described in the well-known product brochures

available from Wako Pure Chem, Inc., or Kayaku Akzo Corporation are used.

[0054]

When the present invention is applied to the
5 production of the (meth)acrylate ester polymer, a chain transfer agent can be added to the reaction vessel so as to adjust a molecular weight of the produced polymer. The chain transfer agent used may be any of a monofunctional chain transfer agent and a multifunctional chain transfer
10 agent. Specifically, the chain transfer agent includes, for example, 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;
15 mercaptans having at most 18 carbon atoms such as ethylene thioglycol; polyhydric alcohols such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol; and an ester produced by esterifying a hydroxyl group with
20 thioglycolic acid or 3-mercaptopropionic acid, 1,4-dihydronaphthalene, 1,4,5,8-tetrahydronaphthalene, beta-terpinene, terpinolene, 1,4-cyclohexadiene and hydrogen sulfide. The above may be used alone or in combination of two or more.

25 [0055]

The amount of the chain transfer agent is not particularly limited, since it varies depending on the types of the chain transfer agent to be used. For example, it is typically in the range from 0.01 to 3 parts by mass, preferably in the range from 0.05 to 1 part by mass based on 100 parts by mass of the raw material monomer, when mercaptans are used. The amount of the above range is preferable, since the mechanical property of the polymer is not spoiled. When two or more chain transfer agents are used in combination, the total usage amount may be within the above range.

[0056]

In the present invention, any of a bulk polymerization method without using a solvent or a solution polymerization method with using a solvent may be used as the polymerization method. The bulk polymerization is particularly preferable.

[0057]

When the polymerization is performed by a continuous solution polymerization method, the polymerization proceeds in the same manner as the continuous bulk polymerization method except that a solvent is used. The solvent to be used for the polymerization reaction, which is suitably selected depending on the raw monomer for the continuous solution polymerization method, and which is not

particularly limited, includes, for example, toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, octane, decane, cyclohexane, decalin, butyl acetate and pentyl acetate. Among them, 5 toluene, methanol, ethylbenzene and butyl acetate are preferable. The solvent can be added to one or both of the initiator composition and the monomer composition, or can be directly introduced to the polymerization reaction vessel 10. Although the ratio of the solvent is not 10 particularly limited, it is preferably in the range from 5 to 30% by mass, more preferably in the range from 1 to 20% by mass based on the total raw material mixture.

[0058]

The above-mentioned polymerization reaction apparatus 15 and the above-mentioned method of producing the polymer by using the polymerization reaction apparatus can sufficiently prevent the raw material monomer and the produced polymer from adhering to the vicinity of the shaft seal bearing part in the polymerization reaction apparatus. 20 Thus, the polymer can be continuously produced for a long period of time without causing the problem associated with the rotation failures of the shaft and the stirring blade.

[0059]

The above-mentioned polymerization reaction apparatus 25 and the above-mentioned method of producing the polymer by

using the polymerization reaction apparatus can be suitably used for producing the (meth)acrylate polymer among polymers, particularly for producing a (meth)acrylate polymer obtained by polymerizing a monomer mixture
5 containing methyl (meth)acrylate as a main component.

[0060]

Since the polymers such as the (meth)acrylate polymer obtained by the above polymerization method has excellent transparency and weather resistance, they can be
10 conveniently used in various fields including illumination, signboards and vehicles. Especially, the (meth)acrylate polymers can be suitably used for materials for an optical disc substrate; optical device materials such as an Fresnel lens, a lenticular lens, a light guide plate used for a
15 back light system of a liquid crystal display, a diffuser plate and a protecting front face plate of a liquid crystal display; and vehicles components such as a tail-lamp covering, a head-lamp covering, a visor and a meter panel.

CLAIMS

1. A polymerization reaction apparatus comprising:

a polymerization reaction vessel for performing a
5 polymerization reaction of a raw material mixture
comprising a monomer;

a stirring blade fixed to a rotatable shaft, which stirs
the raw material mixture within the polymerization reaction
vessel; and

10 a shaft seal bearing part which supports the shaft,
wherein the shaft seal bearing part comprises a shaft
sealing part comprising:

a shaft seal portion (A);

a void portion formed between the shaft seal portion (A)
15 and the polymerization reaction vessel;

a shaft seal portion (B) formed between the void portion
and the polymerization reaction vessel; and

a liquid inlet for introducing a liquid containing a
polymerization inhibitor into the void portion, and

20 wherein the liquid introduced from the liquid inlet is
removed through the void portion into the polymerization
reaction vessel and

wherein the shaft seal portion (B) comprises a lip seal.

25 2. The polymerization reaction apparatus according to

claim 1, wherein the shaft seal portion (A) comprises a mechanical seal.

3. A method of producing a polymer by using the
5 polymerization reaction apparatus according to claim 1 or 2,
comprising a step of:

continuously feeding the raw material mixture containing
the monomer into the polymerization reaction vessel to
carry out the polymerization reaction, while the liquid
10 containing the polymerization inhibitor is introduced into
the void portion through the liquid inlet.

4. The method of producing the polymer according to claim
3, wherein the liquid comprises a mixture of the monomer
15 and the polymerization inhibitor dissolved in the monomer.