

PROCESS FOR PRODUCING METHACRYLIC POLYMER

The present invention relates to a process for producing a methacrylic polymer. In particular, the present invention relates to a bulk polymerization or solution polymerization process for producing methacrylic polymer including a step in which unreacted methacrylic monomer is recycled as a raw material.

Batch-wise suspension polymerization using an aqueous medium is generally used in polymerization of methacrylic monomers. Recently, bulk polymerization or solution polymerization has been increasingly used since it has no accompanying problem of waste water treatment which is associated with use of an aqueous medium, and it has advantages in productivity and energy consumption.

Various proposals have been made on the bulk polymerization of methacrylic monomers, for example, GB 1423288-A, GB 2005282-A, Japanese Patent Publication Nos. 49295/1989 and 26642/1990 and Japanese Patent Kokai Publication No. 111408/1991. The solution polymerization processes of methacrylic monomers are disclosed in Japanese Patent Publication No. 7845/1980 and Japanese Patent Kokai Publication Nos. 132002/1983 and 57613/1988.

In the above bulk polymerization or solution polymerization processes, in general, a polymer composition may contain 30 to 80 % by weight of the polymer of unreacted methacrylic monomers. The unreacted monomers are recovered from a reaction system, and the methacrylic polymer is obtained by separating the unreacted monomers by evaporation. As such devolatilization method, there is known a method using a vented extruder, for example, GB 1467045-A, Japanese Patent Publication No. 53682/1989 and

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Japanese Patent Kokai Publication Nos. 89710/1987 and 49925/1991.

Since the amount of the unreacted monomer contained in the volatile materials which are
5 separated from the polymer composition by evaporation is fairly large in comparison with the amount of the polymer, the unreacted monomer should be reused as raw material in the industrial production. However, when
10 the monomer is continuously reused, the produced methacrylic polymer suffers from property deterioration problems such as colouring of the polymer, decrease of its weather resistance, and the like.

An object of the present invention is to provide
15 a process for producing a methacrylic polymer, which can produce said polymer with good quality, stably and efficiently even when the polymerization is carried out over a long time with continuous reusing of unreacted monomers.

20 This and other objects will become apparent from the following description of the present invention.

The present invention provides a process for producing a methacrylic polymer which comprises bulk or solution polymerizing a methacrylic monomer (a) to
25 obtain a liquid polymer composition (b) containing unreacted methacrylic monomer and separating a volatile component (c) containing said unreacted monomer to obtain said polymer (d), wherein said
volatile component (c) containing said unreacted
30 monomer is treated with a compound having a sulphonic acid group and then with an amine compound, and is recycled to the polymerizing step.

The present invention is described hereinafter, by way of example only, by reference to the annexed
35 drawings, in which;

Fig. 1 is a flow chart of an embodiment of the polymerization process which was used in Examples, and

5 Fig. 2 is a flow chart of another embodiment of the polymerization process.

The methacrylic monomer according to the present invention is methyl methacrylate or a mixture of
10 methyl methacrylate and at least one vinyl monomer copolymerizable therewith.

The methyl methacrylate can be produced by any conventional method, for example, an acetone-cyanohydrin method, a method comprising
15 catalytically oxidizing isobutylene or tert.-butanol to obtain methacrylic acid and esterifying it with methanol, and the like.

Examples of vinyl monomers are methacrylate esters (e.g. ethyl methacrylate, propyl methacrylate,
20 butyl methacrylate, benzyl methacrylate, etc.), acrylate esters (e.g. methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc.), unsaturated carboxylic acids (e.g. acrylic acid, methacrylic acid, maleic acid, itaconic acid, etc.),
25 acid anhydrides (e.g. maleic anhydride, itaconic anhydride, etc.), monomers having a hydroxyl group (e.g. 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglycerol acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, monoglycerol
30 methacrylate, etc.), nitrogen-containing monomers (e.g. acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, diacetoneacrylamide, dimethylaminoethyl methacrylate, etc.), epoxy group-containing monomers (e.g. allyl glycidyl ether,
35 glycidyl acrylate, glycidyl methacrylate, etc.), styrene monomers (e.g. styrene, α -methylstyrene,

etc.),
and the like.

The bulk polymerization itself is well known in the art and is disclosed in GB 1423288-A, GB
5 2005282-A, Japanese Patent Publication Nos. 49295/1989 and 26642/1990 and Japanese Patent Kokai Publication No. 111408/1991.

That is, any polymerization process can be employed in the present invention insofar as the
10 methacrylic monomer is polymerized and the liquid polymer composition containing the unreacted monomer is recovered.

Also, the solution polymerization itself is well known in the art and is disclosed in Japanese Patent
15 Publication No. 7845/1980 and Japanese Patent Kokai Publication Nos. 132002/1983 and 57613/1988.

That is, any polymerization process can be used in the present invention insofar as the methacrylic monomer is polymerized in the presence of an inert
20 solvent and the liquid polymer composition containing the solvent and the unreacted monomer is recovered.

In the present invention, "volatile component" means a substance containing unreacted methacrylic monomer in the bulk polymerization process, or a
25 substance containing unreacted methacrylic monomer and an inert solvent in the solution polymerization process (hereinafter referred to as volatile component).

The separation of the volatile component from the polymer in the liquid polymer composition can be
30 carried out by any one of well known methods, for example, those disclosed in GB 1467045-A, Japanese Patent Publication No. 53682/1989 and Japanese Patent Kokai Publication Nos. 89710/1987 and 49925/1991.

That is, the liquid polymer composition is heated
35 to evaporate the volatile component using a disc or screw type vented extruder, whereby the volatile

component is separated from the polymer.

The separated volatile component is treated with a compound having a sulphonic acid group and then with an amine compound by contacting therewith.

5 The above contact treatment is preferably carried out in the liquid state after said volatile component is condensed, while it may be carried out in the gas state.

10 A part or the whole of the volatile component is treated with a compound having a sulphonic acid group and then with an amine compound either continuously or intermittently. Whether a part or the whole of the volatile component is subjected to the contact treatment or whether the contact treatment is carried
15 out continuously or intermittently is decided according to properties of the obtained polymer, in particular, the colour tone, namely degree of colouring of the polymer. For easy treatment, a part
20 of the volatile component is subjected to the above contact treatment, and a percentage of the volatile component to be treated is adjusted by observing the degree of colouring of the polymer.

The volatile component may contain dimers and/or oligomers and/or a chain transfer agent such as
25 mercaptan which are used in the polymerization. These are preferably removed as "heavies" by distillation before or after the above contact treatment of the volatile component.

30 When water is accumulated in the process, it can be separated from the volatile component by phase separation utilizing the difference of specific gravities.

When the distillation is carried out before the contact treatment, the gaseous volatile component can
35 be directly charged into a distillation apparatus.

Since it is possible that polymerization of the

unreacted monomers continues in the liquefied volatile component, it is preferable to add a polymerization inhibitor to the volatile component at a suitable stage.

5 As the polymerization inhibitor, any of conventional ones which are used for inhibiting polymerization of methyl methacrylate monomers can be used. Examples of polymerization inhibitors are hydroquinone, hydroquinone monomethyl ether,
10 phenothiazine, benzophenothiazine, and the like. The polymerization inhibitor is usually used in a concentration of about 10 to 100 ppm per weight of the unreacted monomer.

 Various solid or liquid compounds may be employed
15 as the compound having a sulphonic acid group to be used in the present invention. Examples of such compounds are sulphuric acid, benzenesulphonic acid, p-toluenesulphonic acid, dioctylsulphosuccinic acid, or strong acidic cation exchange resins such as
20 styrene-divinylbenzene copolymers which have the sulphonic acid group as a functional group.

 The amount of the compound having a sulphonic acid group is usually from 0.0001 to 0.01 equivalent
25 of the sulphonic acid group per one mole of the unreacted monomers.

 The treating time is usually from about 10 to 120 minutes.

 The treating temperature is usually from about 0 to 60°C. When the temperature is too low, the
30 treatment efficiency decreases, while when it is too high, the monomers tend to be hydrolyzed.

 The treating conditions depend on the concentration of impurities and can be easily determined by experimentation.

35 The volatile component may be treated with the compound having a sulphonic acid group by mixing in a

suitable vessel such as an agitating vessel.

Thereafter, the volatile component is separated from the mixture by a conventional liquid-liquid separation method such as phase separation, distillation,

5 evaporation and the like.

Alternatively, when the compound having a sulphonic acid group is a solid compound and insoluble in the volatile component, such as the ion exchange resin, it is placed in a column and the volatile

10 component is passed through the column. This method is preferable since the procedure is simple, the equipment is not corroded, and the unreacted monomer is less hydrolyzed less by this process.

When the volatile component is treated using the packed column, it is passed through the column at a space velocity usually from about 0.1 to 10 hr⁻¹.

After contact with the compound having a sulphonic acid group, the volatile component is treated with the amine compound by contacting

20 therewith.

In the present invention, amine compounds include amines and hydrazines.

It is preferred that the amine compound has a boiling point higher than that of methyl methacrylate.

25 More preferably, it has a boiling point of at least 150°C under atmospheric pressure.

As the amine compound, primary or secondary amines, or hydrazines can be used. Examples of the amine compound in accordance with the present

30 invention are aliphatic amines (e.g. ethanolamine, hexamethylenediamine, octylamine, triethylenepentamine, tetraethylenepentamine, etc.), aromatic amines (e.g. aniline, phenylenediamine, etc.), hydrazines (e.g. hydrazine, phenylhydrazine, etc.), and the like.

35

To treat the volatile component with the amine

compound, any liquid-liquid mixing method can be used insofar as there is intimate contact.

For example, the mixture may be mixed in a vessel equipped with an agitator, or passed through a column having a perforated plate or packings.

Usually, the treating temperature is from room temperature to about 80°C, and the treating time is from about 5 to 120 minutes.

The amount of the amine compound is usually from 0.0001 to 0.01 equivalent per one mole of the unreacted monomers.

The treated volatile component and the amine compound may be separated by any liquid-liquid separation method. In general, they are separated by distillation using a perforated plate column or a packed column.

The distillation step may be carried out only for the separation of the treated volatile component from the amine compound, while it may be carried out together with the removal of the dimer or oligomers and the mercaptans by distillation, or an untreated volatile component may be distilled together with a treated volatile component.

The treated volatile component is mixed with fresh monomer and used in the polymerizing step.

According to the present invention, it is possible to produce the methacrylic polymer having good quality, in particular good colour tone which is one of the important properties of said polymer, even when the unreacted monomer is reused continuously for a long time in either continuous bulk or solution polymerization.

The present invention will now be illustrated by the following non-limiting Examples.

The process used in the Examples is shown in Fig. 1, in which 1 stands for raw material methacrylic

monomer, 2 stands for raw material vinyl monomer, 3 stands for a chain transfer agent, 4 stands for a polymerization initiator, 5 stands for the resulting polymer, 6 stands for waste liquid, 7 stands for an amine compound, "a" stands for a liquid polymer composition, "b" stands for a volatile component, and "c" stands for recovered monomers to be recycled.

The specifications of the main equipment shown in the figures are as follows:

- 10 Monomer preparation vessel:
 20 litres, made of stainless steel SUS 304,
equipped with paddle agitating blades, jacketed.
- Catalyst dissolution vessel:
 10 litres, made of stainless steel SUS 304,
15 equipped with paddle agitating blades, jacketed.
- Polymerization reactor:
 10 litres, made of stainless steel SUS 304,
equipped with helical ribbon agitating blade, jacketed.
- Heater:
20 Inner diameter of 16.7 mm and length of 3 m,
jacketed.
- Vented extruder:
 A twin-screw extruder (TEX-30 manufactured by
Nippon Steel Works Co., Ltd.), different direction
25 rotating type, screw diameter of 30 mm, cylinder
length of 1200 mm, equipped with one rear vent and
three forevents.
- Column for recovering volatile component:
 Inner diameter of 100 mm, length of 3 m, made of
30 stainless steel SUS 304, filled with 3/8 inch Raschig
rings made of stainless steel SUS 304, concentration
part length of 0.7 m, recovering part length of 0.3 m.
- Ion exchange resin column:
 3 litres, made of stainless steel SUS 304, filled
35 with 2 litres of strong acidic ion exchange resin
having sulphonic acid groups (Duolite C-26C

manufactured by Sumitomo Chemical Co., Ltd.).

Amine treating vessel:

1 (one) litre, made of stainless steel SUS 304, equipped with paddle agitating blades, jacketed.

5 Properties of the obtained polymers are evaluated as follows:

(1) Melt flow rate (MFR)

Using a melt flow indexer (manufactured by Takara Industries, Co., Ltd.), a melt flow rate is measured
10 according the JIS K-7210 at 230°C under a load of 3.8 kg.

(2) Degree of colouring

Using a 40 mm extruder having a T die (manufactured by Tanabe Plastics Co., Ltd.), a polymer
15 is extruded at 250°C and passed through three polishing rolls kept at about 100°C to obtain a plate having a thickness of 3 mm.

From the extruded plate, a square plate sample (5 cm x 5 cm) is cut out, and its yellow index (YI) is
20 measured using a spectroscopic colour difference meter SZ-Σ80 (manufactured by Nippon Denshoku Industries Co., Ltd.) according to JIS K-7103.

(3) Weather resistance

The same plate sample as used in the measurement
25 of degree of colouring is irradiated by a sunshine weather meter (WESUN-HCA-1 type manufactured by Suga Testing Machines Co., Ltd.) at 63°C for 2000 hours. Thereafter, the yellow index (YI) is measured and used as a degree of weather resistance.

30 The present invention is further described by the following non-limiting Examples.

Example 1

35 As raw material monomer, methyl methacrylate (hereinafter referred to as "MMA") (manufactured by

Nippon Methacryl Monomer Co., Ltd.) and methyl acrylate (hereinafter referred to as "MA") (manufactured by Toa Synthesis Co., Ltd.) were used. As a polymerization initiator, azobisisobutyronitrile (hereinafter referred to as "AIBN") was used, and as a chain transfer agent, n-octylmercaptan (hereinafter referred to as "OM") was used.

In a catalyst dissolution vessel, MMA, 6.2 % by weight of MA to MMA and 0.12 % by weight of AIBN to MMA were charged and mixed to completely dissolve AIBN in the monomers to prepare a catalyst solution.

An internal temperature of the catalyst dissolution vessel was kept at 5°C by circulating a coolant in the jacket.

The prepared catalyst solution was continuously pumped in a polymerization reactor at a rate of 1.47 kg/hr.

In a monomer preparation vessel, a monomer mixture containing 93.65 % by weight of MMA, 6.2 % by weight of MA and 0.15 % by weight of OM was prepared by controlling supplied amounts of fresh MMA, MA and OM, and a recycled amount and composition of the recovered monomer.

An internal temperature of the monomer preparation vessel was kept at 5°C by circulating a coolant in the jacket.

The prepared monomer mixture was pumped in the polymerization reactor at a rate of 13.279 kg/hr.

From the bottom of the polymerization reactor, the above catalyst solution and the monomer mixture were supplied and polymerized in a residence time of 39 minutes at 150±2°C till an average polymerization degree reached 45 % by weight. The resulting liquid polymer composition was removed from the top of the polymerization reactor and supplied to a heater.

In the heater, the liquid polymer composition was heated up to 200°C by circulating a heating medium in the jacket and pressurized to $20\text{ kg/cm}^2\text{G}$ and then introduced in a vented extruder.

5 The liquid polymer composition was passed through the extruder while keeping each vent under reduced pressure, and a cylinder temperature at about 250°C , and the volatile component was recovered from the vents and supplied to a column for recovering volatile
10 component.

The polymer in a molten state was extruded in a strand form. After cooling with water, the strand was cut to obtain pellets at an average production rate of 6.65 kg/hr .

15 The gas state volatile component recovered from the rear vent of the extruder was supplied in the recovering part of the column for recovering volatile component, while the volatile component recovered from the forevents of the extruder was cooled and condensed
20 to form liquid, and then supplied to the bottom of column for recovering volatile component, where the volatile component was continuously distilled at a reflux ratio of 1.

From the effluent recovered from the top of the
25 column for recovering volatile component, an average of 7.98 kg/hr on the average was recycled to the monomer preparation vessel, while 1 kg/hr of the distilled liquid was supplied to the subsequent ion exchange resin column.

30 From the bottom of the column for recovering volatile component, a waste liquid containing an amine which was used in the amine treatment step and a reaction product of the amine and impurity was drained at an average rate of 147 g/hr .

35 To the top of the column for recovering volatile component, hydroquinone (a polymerization inhibitor)

was continuously supplied at a rate of about 0.5 g/hr.

The effluent from the column for recovering volatile component was continuously passed through the ion exchange resin column at an average rate of 1 kg/hr. In this step, a space velocity was about 0.5 hr⁻¹.

To the effluent from the ion exchange resin column, tetraethylenepentamine was continuously supplied at a rate of 2 g/hr and the mixture was flowed into an amine compound treating vessel. The monomers and the amine were mixed in the vessel for an average residence time of about one hour while keeping an internal temperature at 50°C by heating the vessel with the jacket.

The liquid flowing out from the amine compound treating vessel was supplied to the bottom of the column for recovering the volatile component.

The above continuous operation was continued for 30 days, and samples of the polymer obtained after 10 days, 20 days and 30 days were subjected to the property evaluation.

Each polymer had a melt flow rate of 1.5, Yl of 0.4, and a weather resistance of 0.7 in terms of Yl.

Example 2

A polymer was prepared in the same manner as in Example 1, except that octylamine was supplied to the amine treating vessel in place of tetraethylenepentamine.

Each polymer had a melt flow rate of 1.5, Yl of 0.4 and a weather resistance of 0.7 in terms of Yl.

Example 3

5 A polymer was prepared in the same manner as in
Example 1 except that the concentration of MA in the
catalyst dissolution vessel was adjusted to 10.5 % by
weight, and the concentrations of MMA, MA and OM in
the monomer preparation vessels were adjusted to 89.03
% by weight, 10.51 % by weight and 0.46 % by weight,
10 respectively.

Each polymer had a melt flow rate of 20, Yl of
0.4 and a weather resistance of 0.7 in terms of Yl.

Comparative Example 1

15

A polymer was prepared in the same manner as in
Example 1 except that the whole amount of effluent
from the top of column for recovering volatile
component was recycled directly to the monomer
20 preparation vessel without further treatment.

The properties of the polymers are shown in Table
1.

Comparative Example 2

25

A polymer was prepared in the same manner as in
Example 1 except that no amine was added to the
effluent from the ion exchange resin column, that is,
the amine treatment was not carried out.

30 The properties of the polymers are shown in Table 1.

35

Comparative Example 3

5 A polymer was prepared in the same manner as in
Example 1 except that the effluent from the column for
recovering volatile component was directly supplied to
the amine treating vessel, that is, the treatment in
the ion exchange resin column was skipped.

10 The properties of the polymers are shown in the
Table 1.

15

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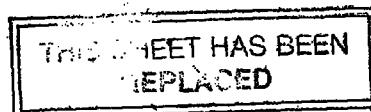
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TABLE 1

Comparative Example Number		MFR	YI	Weather resistance
1	After			
	10 days	1.5	3	7
	20 days	1.5	7	>15
	30 days	1.5	10	>15
2	After			
	10 days	1.5	1.5	3
	20 days	1.5	3	7
	30 days	1.5	6	>15
3	After			
	10 days	1.5	2	5
	20 days	1.5	5	12
	30 days	1.5	7	15



CLAIMS

1. A process for producing a methacrylic polymer
5 which comprises bulk or solution polymerizing a
methacrylic monomer (a) to obtain a liquid polymer
composition (b) containing an unreacted methacrylic
monomer and separating a volatile component (c)
10 containing said unreacted monomer to obtain said
polymer (d), wherein said volatile component (c)
containing said unreacted monomer is treated with a
compound having a sulphonic acid group and then with
an amine, and is recycled to the polymerizing step.
- 15 2. A process according to claim 1, wherein said
volatile component (c) containing said unreacted
monomer is distilled before it is treated with said
compound having a sulphonic acid group.
- 20 3. A process according to claim 1, wherein said
volatile component (c) containing said unreacted
monomer is distilled after it is treated with said
amine.
- 25 4. A process according to any one of claims 1 to 3
wherein said compound having a sulphonic acid group is
a cation exchange resin having sulphonic acid groups.
5. A process according to any one of claims 1 to 4,
30 wherein said amine is a primary or secondary amine
having a boiling point of at least 150°C under
atmospheric temperature.
6. A process according to claim 1 substantially as
35 described in Example 1, 2 or 3.

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