

-1-

PROCESS FOR PRODUCTION OF METHACRYLATE POLYMERS

This invention relates to a continuous process
5 for producing methacrylate polymers in the manner of bulk
polymerization.

Methacrylate polymers are used in a broad range
of molding applications ^{which take} ~~by taking~~ advantage of their
10 characteristically high clarity, gloss, surface hardness,
weather resistance and mechanical properties. Recently,
these polymers have come to be used in large quantities
in optical applications, e.g. optical disk substrates and
optical devices such as Fresnel and lenticular lenses,
15 among others.

^{the} For ~~a~~ commercial-scale production of such
methacrylate polymers, suspension polymerization, bulk
polymerization and solution polymerization techniques are
known. The bulk polymerization method, for instance,
20 includes the time-honored versions represented by the
cell casting process wherein a monomer is polymerized in
a cell or mold to give a resin of the desired shape, e.g.
in the form of a plate, in one operation.

Recently, for the production of molding
25 materials, processes have been proposed which comprise

10
043

10
043

10
043

function of said polymerization temperature.

~~JP-B- Japanese Examined Patent Publication (Kokoku)~~

No. H2-26642 also discloses a process for producing a methacrylate resin by bulk polymerization wherein the
5 type and amount of the radical initiator used are controlled within the range satisfying a certain relation with the half-life thereof at a polymerization temperature and the polymerization reaction is conducted at 160-200°C while the viscosity of the reaction system at the
10 polymerization temperature is maintained at 10-500 poises.

~~JP-A- Japanese Unexamined Patent Publication (Kokai)~~

No. H3-111408 discloses a process for producing a methacrylate polymer from a monomer mixture composed
15 predominantly of methyl methacrylate using a thorough-mixing type reactor wherein an inert gas is first bubbled through the monomer to reduce the dissolved oxygen level in the monomer to 1 ppm or less and the polymerization reaction is carried out in the presence of a radical
20 initiator having a half life of 0.5-120 seconds at a polymerization temperature with stirring using a stirrer providing for a stirring power of 0.5-20 kW per m³ of the reaction mixture in such a manner that the ratio of half life of the radical initiator to average residence time
25 will be 1/200 to 1/10,000 and that the conversion will be

efficiency of heat removal, thereby interfering with the reaction temperature control and further causing the impeller blades to come into contact with the polymer deposit grown within the reactor so that a long-term
5 stable production run becomes difficult.

Furthermore, said polymer film is exfoliated and contaminates the reaction system, leading to production of inhomogeneous methacrylate polymer.

With the method utilizing the latent heat of
10 evaporation of the monomer, it is essential to provide a gas phase within the reactor so as to permit vaporization of the monomer, and a fairly large amount of polymer deposit is formed on the reactor wall corresponding to the gas phase and the interface between the gas phase and
15 the liquid phase, and these deposits tend to come off, resulting in inhomogeneity of the product methacrylate polymer.

In addition, the polymerization conditions described in the above ~~Japanese Examined Patent~~
~~Publications (Kokoku) Nos. 52-32665 and H2-26642 and~~
20 ~~Japanese Unexamined Patent Publication (Kokai) No. H3-~~
111408 utilize the development of the so-called self-accelerating effect (gel effect) of the polymerization reaction. Such polymerization reactions tend to be
25 easily affected by extrinsic disturbances such as the

effect of the dissolved oxygen present in the monomer, among others, so that sophisticated control of heat removal is necessary for constantly conducting a stable polymerization reaction for a long period of time.

5 It is therefore an object of this invention to provide a process for producing a methacrylate polymer, which is capable of achieving a high conversion even when the monomer residence time in the reactor is short, and therefore capable of achieving a high polymer yield per unit
10 reactor volume, namely high productivity, and by which polymer type or grade is easily changed with a reduced amount of carryovers.

 It is a further object of this invention to provide a process for producing a methacrylate polymer which
15 can provide for stable polymerization even in the presence of extrinsic disturbing factors such as the effect of dissolved oxygen in the monomer, which can remarkably suppress oligomer formation, which involves substantially no formation of deposit on the reactor wall even in a long
20 production run and which can give a homogeneous methacrylate polymer.

 The invention accordingly provides a process for producing a methacrylate polymer composition having a polymer content of 40-70% by weight, which process comprises
25 continuously polymerising a monomer feed composed predominantly of methyl methacrylate in a bulk polymerisation reactor of the ^{perfect}~~complete~~ mixing type, the reactor being substantially full up with the polymer

The polymer composition means the content present in the bulk polymerization reaction system of the invention, and comprises a methacrylate polymer formed by the bulk polymerization and fed or unreacted monomer or
5 monomer mixture, the methacrylate polymer being present in an amount of 40-70 % by weight based on the total weight of the composition.

Said polymer composition is sometimes referred to as "liquid polymer composition", "syrup" or
10 "polymerization mixture" in the description that follows.

The term "monomer feed composed predominantly of methyl methacrylate" as used throughout this specification and claims appended thereto means methyl methacrylate as such or a mixture of at least 70 weight
15 %, preferably at least 80 weight %, of methyl methacrylate and up to 30 weight %, preferably up to 20 weight %, of at least one of other vinyl monomers copolymerizable with methyl methacrylate.

Insertion of a
paragraph

"Typically
the monomer...
-- the methyl
methacrylate"

20 Said other vinyl monomers copolymerizable with methyl methacrylate includes, for example, other esters of methacrylic acid such as ethyl methacrylate, propyl methacrylate, butyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, etc.; esters of acrylic acid such as methyl acrylate, ethyl acrylate, propyl acrylate,
25 butyl acrylate, 2-ethylhexyl acrylate, etc.; unsaturated

carboxylic acids and anhydrides thereof, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride, itaconic anhydride, etc.; hydroxy group-containing monomers such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglyceryl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, monoglyceryl methacrylate, etc.; nitrogen-containing monomers such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, diacetone acrylamide, dimethylaminoethyl methacrylate, etc.; and epoxy group-containing monomers such as allyl glycidyl ether, glycidyl acrylate, glycidyl methacrylate, etc., and styrenic monomers such as styrene, α -methylstyrene and so on.

In the present invention, the bulk polymerization is conducted in a continuous manner.

The polymerization reactor to be used in the practice of this invention is a vessel type reactor equipped with a stirring means. The ^{said} stirring means ~~just~~ ^{perfect} ~~mentioned~~ is one capable of achieving ~~a complete~~ mixing of the liquid contents within the reaction vessel. The shape of the stirrer blade that can be adopted is not particularly limited so far as it achieves perfect mixing. Examples thereof include Max Blend* blade (tradename; product of Sumitomo Heavy Industries, Ltd.),

* Registered Trademark

paddle blade, double helical ribbon blade, MIG
(Mehrstufen-Impuls-Gegenstromruehrer) blade, Fullzone*
blade (tradename; product of Shinko Pantec Co., Ltd.),
etc.

5 For enhanced stirring effects, it is preferable
to install one or more baffles.

Needless to say, the stirring efficiency is
preferably as high as possible, but the use of a stirring
power greater than necessary should be avoided, since it
10 would only contribute to accumulate additional heat in
the reaction vessel.

For this reason, the stirring power is usually
in the range of about 0.5 to 20 kW/m³, preferably 1 to 15
kW/m³. As the viscosity of the reaction mixture, i.e./
15 the polymer content, ~~therein~~ increases, the stirring
power is usually increased.

The interior of the reaction vessel is filled
up, leaving substantially no gas phase. This absence of
gas phase prevents the formation and buildup of the
20 polymer deposit on the reactor internal wall surface
corresponding to the gas phase and gas-liquid interface
which would otherwise exist, and consequently
deterioration of the product polymer quality due to
contamination with such deposit is prevented.

25 Furthermore, the full capacity of the reactor

* Registered Trademark

can be utilized with the result that ~~the~~ productivity increases.

The most expedient method for filling up the reactor is to dispose the reaction mixture outlet at the highest part of the reactor. For ensuring that no monomer gas be evolved in the reactor, the internal pressure of the reactor is set above the vapor pressure thereof at ~~the~~ ^{the} temperature of the reaction system. This pressure is generally about 10-20 kg/cm².

10 In the practice of this invention, the reactor is kept substantially insulated thermally so that there will be no exchange of heat between the reactor interior and the external atmosphere. In other words, the reactor exterior wall is maintained at a temperature which is
15 substantially the same as the temperature of ^{the} interior of the reactor.

For achieving this substantial thermal insulation, a jacket is installed, for example, on the external wall of the reactor and a heating medium such as
20 steam is circulated through the jacket in such a manner that the external wall temperature of the reactor will follow the internal temperature and remain substantially the same as the internal temperature. Such temperature control can be easily conducted by one skilled in the
25 art, for example, by using a system conventionally used

for effecting such temperature control.

Maintenance of

~~To maintain~~ the reactor in a thermally

insulated state as mentioned above is intended to prevent

the formation of polymer deposits on the internal wall of

5 the reactor and to achieve a self-control function which

stabilizes the polymerization and suppresses a runaway or uncontrollable reaction.

There is no point in increasing

~~it is meaningless to increase~~ the external wall

temperature of the reactor too high beyond the reaction

10 mixture temperature, since ~~it~~ ^{this} would add an unnecessary heat to the reaction mixture.

The temperature difference between the interior of the reactor and the external wall of the reactor is preferably as small as possible, but ^{in practice} ~~actually~~ it is

15 sufficient to control the reactor interior temperature

and the reactor exterior wall temperature in such a ~~that~~ ^{between them} manner

~~that the temperature difference is approximately~~ ^{about} less than _A5 degrees (°C).

The heat evolved in the reaction zone, that is to say, the heat of polymerization plus the heat of agitation, is balanced against the heat carried away by the syrup emerging out of the reactor and the feed monomer temperature (sensible heat), ^T ~~so that~~ the polymerization reaction temperature can ^{thus} be maintained

25 within the range of 120 to 180 °C.

The heat carried away by the syrup is dependent on the amount and specific heat of the syrup and the polymerization temperature.

The polymerization temperature, which is
5 dependent on the type of radical initiator used and the like, is about 120-180°C, preferably 130-170°C.

If the polymerization temperature is too high, the syndiotactic structure of the product polymer tends to decrease, and the proportion of oligomers increases,
10 and the heat resistance of the resin is sacrificed.

In feeding the monomer to the reactor, the temperature of the monomer is controlled so that a predetermined polymerization temperature will be established by the heat balance within the reactor.

15 ~~In other words,~~ ^Tthe feed monomer temperature T^1 ~~is~~ ^{may thus be} set within the range defined by the following relation (3):

$$T^1 = (0.8 \text{ to } 1.2) \times \{T - (2.9P + 1.81F)\} \quad (3)$$

wherein P represents conversion in %, F represents
20 stirring power in kW/m^3 , and T represents polymerization temperature in °C.

In the above relation (3), 2.9 is the conversion factor for a reaction temperature increase per weight % of conversion and 1.81 is the conversion factor
25 for a temperature increase per kW/m^3 of stirring power.

The monomer to be fed to the polymerization reactor need not be limited to a fresh monomer, but may be an adjusted composition containing the recovered unreacted monomer(s).

5 To preclude the influence of dissolved oxygen in the preparation of the monomer, it is conventionally common practice to bubble an inert gas through the monomer preparation tank or ^{to decrease} ~~deacerate~~ the monomer under decompression in order to remove dissolved oxygen
10 therefrom. However, the process of this invention does not require such a procedure in ^a strict sense, and the desired polymerization can be carried out in a stable manner even if the dissolved oxygen level in the monomer is about 1.5 - 3 ppm.

15 For the purpose of removing impurities before introducing the prepared monomer feed into the reactor, *the product of the invention may include the preliminary step of passing* the monomer feed ~~is preferably filtered~~ through a filter *before* ~~introducing it into the reactor. The filter is~~ of the proper mesh size, and this is especially desirable when the product polymer is intended for use as an
20 optical material.

The average residence time is about 15 minutes to about 2 hours, preferably about 20 minutes to about 1.5 hours.

The average residence time is defined by the
25 following equation

$$\theta = V/F$$

wherein θ is average residence time in minute, V is a capacity of the reactor in ^{liters} ~~liter~~ and F is a monomer feed rate in ^{liters} ~~liter~~/minute. In the invention, the specific gravity of the monomer or monomer mixture and the specific gravity of the polymer composition (syrup) are usually in the neighborhood of 1, and therefore can substantially reasonably be assumed to be 1 for calculating the average residence time θ . If the residence time is excessively prolonged, the formation of ~~the dimers, trimers and other oligomers~~ is increased. ~~to this thereby detracts~~ from the heat resistance of the resulting product. The average residence time can be controlled by adjusting the monomer feeding rate per unit time.

15 The radical initiator for use in the ^{present} ~~practice~~ of ~~this~~ ^{the present} invention is ~~virtually~~ not limited in type, ^{but preferably} ~~only~~ if its half life at the polymerization temperature is not in excess of 1 minute/ and is ^{more preferably} ~~particularly~~ in the range of 0.01 second to 1 minute.

20 Any radical initiator with a half life of over 1 minute is undesirable because the reaction rate will then be low.

The relationship between the temperature and the half life of the radical initiator can be found in 25 the literature on respective initiators and ~~the~~ technical

monocarbonate, 1,1,3,3-tetramethylbutyl peroxyiso-
propylmonocarbonate, 1,1,2-trimethylpropyl peroxy-
isopropylmonocarbonate, 1,1,3,3-tetramethylbutyl peroxy-
isononanoate, 1,1,2-trimethylpropyl peroxyisononanoate,
5 t-butyl peroxybenzoate, 1,1-bis(tert-butylperoxy)-3,3,5-
trimethylcyclohexane, 1,1-bis(tert-butylperoxy)-
cyclohexane, etc. One or more of these polymerization
initiators is(are) used according to the polymerization
temperature.

10 The concentration C of the radical initiator
(mol/100 g monomer) for use in the process of this
invention is suitably selected according to the
aforementioned relation (1). If the concentration of the
radical initiator is below the lower limit defined by
15 relation (1), the desired conversion will not be
attained. Conversely when the initiator concentration is
too high, the resulting polymer will ^{possess} ~~be~~ insufficient ~~in~~
thermal stability.

 The concentration of the initiator is generally
20 0.001-1 weight % based on the monomer feed.

 The radical initiator is usually fed to the
reactor ~~as~~ dissolved in the monomer.

 It is preferable that the concentration C of
the radical initiator (mol/100 g monomer) is within the
25 range satisfying the following relation (2):

$$4 \times 10^{-5} \cdot \exp(0.019T) < C \cdot \Theta < 3 \times 10^{-5} \cdot \exp(0.034T) \quad (2)$$

where Θ and T are as defined hereinbefore.

In the bulk polymerization according to this invention, the selection of the reaction conditions according to the above description leads to the self-accelerating effect (gel effect) in the radical polymerization, which can stably impart a favorable effect to the polymerization reaction.

Generally, the gel effect develops in a solution (monomer/polymer/(solvent)) having a fairly high polymer content. Thus, when the polymer content is high, the viscosity of the solution is high and therefore the mobility of the polymer radicals is decreased with the result that the polymerization rate is increased because the termination reaction ~~is hard to~~ ^{cannot readily} occur.

Therefore, ~~inherently~~ a runaway reaction tends to take place. In order to avoid this uncontrollable reaction, it has been conventionally necessary to ~~very elaborately~~ control the residence time, reaction temperature and radical initiator concentration, *very elaborately*.

However, in the process of this invention, such a runaway reaction is inhibited by simply conducting the polymerization in such a manner that there is substantially no temperature difference between the interior and exterior of the reactor to establish a

thermally insulated state with substantially no exchange of heat with the external environment, ~~and therefore~~ ^Tthe polymerization, ~~therefore~~ proceeds in a stable manner.

Thus, even if a transient increase in the
5 evolution of heat raises the internal temperature of the reactor, the temperature of the exterior wall of the reactor is also increased accordingly so that the viscosity of the reaction mixture is lowered with the result that the mobility of the polymer radicals is
10 increased to enable the termination reaction to occur frequently. Therefore, the total polymerization rate is lowered and the evolution of heat is reduced to lower the temperature, thus resulting in a conversion commensurate with the concentration of the radical initiator, thus
15 developing said self-control function.

As a consequence, a consistently stable polymerization reaction can be carried out even if external disturbances such as fluctuation in the dissolved oxygen level in the monomer occur.

20 The conversion from the monomer to the polymer in the reactor is 40-70 weight %. Because the content of the reactor is maintained in a substantially perfect mixing state, this conversion corresponds to the polymer content of the syrup emerging out of the reactor. That
25 is to say, the conversion is equal to the concentration

of the polymer in the syrup.

Higher conversion means not only higher productivity, but also ~~the~~ increased viscosity of the reaction system, and requires a greater stirring force.

5 On the other hand, the lower the conversion is, the larger is the unreacted monomer recovery load.

The reaction parameters mentioned hereinbefore can be readily selected by one skilled in the art. For example, the concentration of the radical initiator and
10 the amount of the monomer feed to be introduced into the reactor may be calculated as follows.

When the amount of the polymer to be produced is predetermined, a target for the residence time θ and a target for the polymer content in the syrup are selected,
15 and the target polymerization temperature is selected. Then the temperature range of the monomer feed is roughly estimated according to relation (3) using the above polymer content and the polymerization temperature values and further using the stirring power value which is
20 roughly assessed from these values. Thereafter, the concentration range of the radical initiator is calculated according to relation (1).

So far as the radical initiator concentration is within said range calculated according to relation (1)
25 and the reactor is kept substantially insulated

thermally, the reaction would never run away or become uncontrollable. However, it is generally preferable to start and conduct the reaction as follows. First, the radical initiator is fed at approximately the lowest
5 level in the initiator concentration range. Then, with an increase in the internal temperature, the jacket temperature is correspondingly elevated to maintain the state of thermal insulation until the temperature reaches an equilibrium state. The initiator concentration is
10 adjusted so as to achieve an equilibrium at the target temperature. When the amount of the polymer that is produced does not reach the predetermined level, the amount thereof can be controlled by adjusting the initiator concentration within the above range.

15 In order to control the molecular weight of the product polymer, *a chain transfer agent may be used. This is, for instance,* a conventional monofunctional or polyfunctional chain transfer agent. ~~can be employed, if so desired.~~

The chain transfer agent that can be used *mercaptans, for instance*
20 includes, alkylmercaptans such as propyl mercaptan, butyl mercaptan, hexyl mercaptan, octyl mercaptan, 2-ethylhexyl mercaptan, dodecyl mercaptan, etc.; aromatic mercaptans such as phenyl mercaptan, thiocresol, etc.; mercaptans containing not more than 18 carbon atoms, such as
25 ethylenethioglycol, and thioglycolic or 3-

mercaptopropionic esters of polyhydric alcohols such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, etc.

5 Also, 1,4-dihydronaphthalene, 1,4,5,8-tetrahydronaphthalene, β -terpinene, terpinolene, 1,4-cyclohexadiene, ~~1,4-cyclohexadiene~~ ⁷ α -methylstyrene dimer, hydrogen sulfide, etc. can likewise be employed.

 These agents can be used singly or at least 2
10 of them may be used in combination.

 The amount of such chain transfer agent varies with different kinds of agents but taking a mercaptan as an example, the proper amount is, ^{typically} 0.01 to 3 parts by weight, preferably 0.05 to 1 part by weight, per 100
15 parts by weight of the monomer or monomer mixture. The above range is recommended because the mechanical properties of the polymer are not adversely affected and a sufficiently high heat stability of the polymer is maintained.
 ^{Insert "In one aspect withdrawn polymer composition."}
20 The syrup withdrawn from the reactor is preheated, if required, to evaporate off the volatile matter which is predominantly composed of unreacted monomer, leaving the desired polymer.

 For this transfer of the syrup, the method
25 described in ~~Japanese Examined Patent Publication~~

~~JP-B-~~
(~~Kokoku~~) No. H4-48802 is suitable.

The technique for separation of the volatile matter includes the method employing a devolatilizing extruder, and the known techniques described in Japanese

~~JP-B-~~
5 ~~Examined Patent Publications (Kokoku) Nos. 51-29914 and~~
~~JP-B-~~
52-17555, ~~Japanese Unexamined Patent Publications (Kokai)~~
~~JP-A-~~ ~~JP-A-~~ ~~JP-B-~~
Nos. H1-53682, H2-89710 and H3-49925, among others, can be utilized.

The unreacted monomer thus separated can be
10 reused as the feed monomer for polymerization.

In this connection, the impurities contained in the unreacted monomer, such as compounds contaminated or by-produced in the monomer manufacturing processes, the dimers, trimers and other oligomers and the residue
15 (decomposition product) of the radical initiator, accumulate progressively, whereby the resulting polymer will be colored. It is, therefore, recommended to remove the impurities by distillation or adsorption as disclosed
~~JP-B-~~
in ~~Japanese Examined Patent Publication (Kokoku) No. 54-~~
20 42035.

According to the invention, as applied to the production of a methacrylate polymer by the continuous bulk polymerization of a monomer feed composed predominantly of methyl methacrylate in a thorough mixing
25 type reactor, a long-term polymerization run can be

c : recovered monomers to be recycled

The following are generalized descriptions of the main equipment used in the Examples which follow.

- Monomer preparation tank: 20L, SUS304, equipped
5 with a paddle agitator and a jacket
- Initiator dissolution tank: 10L, SUS304, equipped
with a paddle agitator and a jacket
- Polymerization reactor: 10L, SUS304, equipped with
a double helical ribbon blade stirrer (250 rpm)
10 and a jacket
- Heater: 16.7 mm (inside diameter) x 3m (long),
equipped with a jacket
- Devolatilizing extruder: a twin screw extruder
(TEX-30) manufactured by The Japan Steel Works,
15 Co., Ltd. (different direction rotating type,
screw diameter 30 mm, cylinder length 1200 mm),
equipped with one rear vent and 3 front vents
- Monomer recovery column: 100 mm (inside diameter) x
3m (long), SUS304, ^{4.72mm} (3/8 inch) SUS Raschig ring-
20 packed column, concentration part length 0.7 m,
recovering part length 0.3 m.
- Dissolved oxygen concentration meter: DO Meter UC-
12-SOL manufactured by Central Kagaku Co., Ltd.

The methods used for the evaluation of product

Claims

1. A process for producing a methacrylate polymer composition having a polymer content of 40-70% by weight, which process comprises continuously polymerising a monomer feed composed predominantly of methyl methacrylate in a bulk polymerisation reactor of the ~~complete~~^{perfect} mixing type, the reactor being substantially full up with the polymer composition and being maintained in a thermally insulated state, at a polymerization temperature of from 120 to 180°C with an average residence time of 15 minutes to 2 hours, using a radical initiator which has a half-life of not more than 1 minute at the polymerization temperature at a concentration C (mol/100 g monomer) which satisfies the following relation:

$$4 \times 10^{-5} \cdot \exp(0.019T) < C \cdot \theta < 3 \times 10^{-8} \cdot \exp(0.079T) \quad (1)$$

wherein θ is the average residence time (minutes) and T is the polymerization temperature (°C).

2. A process according to claim 1, wherein the concentration of the radical initiator C (mol/100 g monomer) satisfies the following relation:

$$4 \times 10^{-5} \cdot \exp(0.19T) < C \cdot \theta < 3 \times 10^{-5} \cdot \exp(0.034T)$$

wherein θ and T are as defined in claim 1.

3. A process according to claim 1 or 2, wherein the monomer feed comprises from 70-100% by weight of methyl methacrylate and from 0-30% by weight of a vinyl monomer or of a blend of two or more vinyl monomers, the vinyl monomer or monomers being copolymerizable with methyl methacrylate.

4. A process according to any one of claims 1 to 3,
wherein the reactor interior temperature and the reactor
exterior wall temperature are controlled such that the
temperature difference between them is ^{less} ~~no more~~ than about
5 5°C.

5. A process according to any one of the preceding
claims, wherein the polymerization temperature is from 130
to 170°C.

6. A process according to any one of the preceding
10 claims, wherein the average residence time is from 20
minutes to 1.5 hours.

7. A process according to any one of the preceding
claims, wherein the stirring power in the reactor is from
0.5 to 20 kW/m³.

15 8. A process according to any one of the preceding
claims, wherein the pressure within the reactor is from 10
to 20 kg/cm².

9. A process according to any one of the preceding
claims, wherein the radical initiator is used in an amount
20 of 0.001 to 1 % by weight based on the monomer feed.

10. A process according to any one of the preceding
claims, wherein a chain transfer agent is used.

11. A process according to claim 10, wherein the chain
transfer agent is a mercaptan.

25 12. A process according to claim 11, wherein the
mercaptan is used in an amount of 0.01 to 3 parts by weight
per 100 parts by weight of the monomer or monomer mixture.

13. A process according to any one of the preceding

claims which includes the preliminary step of passing the monomer feed through a filter before introducing it into the reactor.

14. A process according to any one of the preceding
5 claims which further comprises continuously withdrawing the polymer composition from the reaction zone and, optionally, continuously removing volatile components from the withdrawn polymer composition.

15. A methacrylate polymer composition whenever
10 produced by a process as claimed in any one of claims 1 to 14.

16. A continuous bulk polymerization process for
producing a methacrylate polymer composition having a
methacrylate polymer content of from 40-70% by weight, the
15 process being substantially as hereinbefore described in any one of Examples 1 to ⁶/₇.