

Copolymer based on methyl methacrylate and optical grade moulding composition comprising it

The present invention is directed to copolymers based on methyl methacrylate and a norbornene type monomer having increased heat resistance, high transparency and low haze values. Further, the invention relates to moulding compositions comprising the inventive copolymer and to a process for easy production of the inventive copolymer by radical polymerisation. The moulding compositions of the present invention are highly suitable for the manufacturing of moulded articles, that can be used as optical elements in various optical devices, e.g. as light guides or lamp covers.

10 Prior art

Copolymers comprising repeating units derived from methyl methacrylate (hereinafter MMA), which, for the sake of simplicity are often called polymethyl methacrylate (hereinafter PMMA), are usually transparent materials having a high weathering resistance, in particular, a high resistance against solar UV radiation. If desired, weathering resistance of PMMA can be even further increased by addition of UV absorbers, stabilizers and inhibitors. Hence, PMMA is commonly used in applications where high transparency, low haze and high weathering resistance are required.

There is also a growing demand for polymers with particularly high heat resistance for optical applications. These applications include e.g. light sources for indoor and outdoor use comprising high-power LEDs, where such polymers are used as light guides, optical lenses *etc.* In order to increase the light yield of the LEDs, the optical elements are positioned in a close proximity to the LED. Operating temperature of the LED surface, especially of so-called white high-power LEDs, often exceeds 100 °C or sometimes even 130 °C. Accordingly, it is important that materials for these applications have a high transparency and particularly low haze values as well as a high thermal stability. Additionally, the materials should have a high weathering stability and show substantially no signs of yellowing upon a long-term exposure to solar radiation.

Several copolymers comprising methyl methacrylate (MMA) having improved heat stability are described in the state of the art. For example, WO 2022/122806 A1 describes a copolymer of methyl methacrylate, (meth)acrylic acid and optional co-monomers and a process for producing it, wherein the copolymer and moulding compositions comprising it, should have a high heat resistance and low content of glutaric anhydride units. Further, the documents WO 2021/219738 and WO 2017/097979 A1 describe copolymers of MMA and methacrylic acid as well as processes for their production. Said copolymers typically show Vicat temperature of about 116 °C. In order to increase the Vicat temperature of said copolymers up to 120 °C and higher it would be necessary to increase the amount of methacrylic acid units. However, higher amounts of methacrylic acid units leads to insufficient processability and higher water absorption. Generally, water absorption reduces the Vicat softening temperature of the polymer.

Further, copolymers of MMA, maleic anhydride and styrene are known from the state of the art. For example, WO 2005/108486 A1 and WO 2020/126722 A1 describe such copolymers and blend comprising said copolymer. Often the transparency of said copolymers and blends is not sufficient for several optical applications. An additional disadvantage is that the presence of styrene typically impairs the weathering resistance.

Imidated poly alkyl (meth) acrylate, such as poly methyl meth acrylimide (PMMI) are also known in the state of the art (e.g. WO 2009/135703 A1). Typically, PMMI shows high heat resistance including Vicat temperature of about 120 °C and higher, however the production of said imidated polymers is elaborated and costly and the optical properties, such as transmission and yellowness, are often not sufficient for several optical applications requiring high standards. Additionally, it is disadvantageous that the moisture absorption of PMMI is high due to the meth acrylimide groups, and typically, the Vicat temperature of a polymer or polymer blend having high moisture content is reduced.

It is known from the state of the art that radical copolymerisation of norbornene and alkyl (meth) acrylates includes several difficulties. It is reported that radical copolymerisation of norbornene with methyl acrylate may be carried out in solution polymerisation applying long reactions times of 20 hours (see comparative example 1, KR 2009/0020344 A). Further, radical copolymerisation of norbornene and acrylate monomers, such as methyl acrylate, tert-butyl acrylate and acrylic acid, using benzoyl peroxide as initiator is described in "*Copolymers of norbornene and its derivatives with acrylates-Promising materials for optoelectronics*", Bykov, V. I. et al, Doklady Chemistry, 2011, Vol. 439, Part 2, pp. 227–229. The document RU 2 456 304 C2 describes radical copolymerisation of an acrylate monomer, in particular methyl acrylate, and norbornene. For example, the copolymer may be prepared by polymerisation of a monomer mixture with monomer ratio of norbornene : methyl acrylate of 3:1 to 1:1 mol/mol at a temperature of 25 to 30 °C in the presence of a radical initiator (e.g. benzoyl peroxide). Contrary, it is described that free radical copolymerisation of norbornene with methyl methacrylate (MMA) does not lead to incorporation of NB into the polymer chain (see comparative example 2, JP H04 63810 A), particularly due to the sterically hinderance of the alpha positioned methyl group.

The publication Yeh An-Chi, "Free Radical-Induced Copolymerization of Norbornene and Methacrylate", 31 December 2008 (2008-12-31) (URL: https://www.jofamericanscience.org/journals/am-sci/0401/13_0401_yeh_am.pdf) describes the preparation of norbornene-methacrylate copolymers formed by free radical polymerisation using N,N'-azobisisobutyronitrile (AIBN) initiator. Said copolymers exhibit relative low molecular weight below 30.000 g/mol and can be used for preparing thin optically transparent films.

It is known that norbornene can be radically copolymerized with electron-deficient monomers, such as maleic anhydride, for example in "*Fundamental Aspects of Norbornene-Maleic-Anhydride Co and Terpolymers for 193 nm Lithography: Polymerization Chemistry and Polymer Properties*", Hiroshi Ito et al., Journal of Photopolymer Science and Technology, 2000, p. 559-589. Furthermore, the radical

terpolymerisation of norbornene, maleic anhydride and methacrylic monomers, such as tert-butyl acrylate or methacrylic acid, is described in Hiroshi Ito et al. For example, terpolymers of MMA, norbornene, and an electron-deficient co-monomer, such as maleic anhydride, maleimide or N-cyclohexylmaleimide, or vinyl chloride, and their synthesis via radical polymerisation, are described in WO 2021/259965 A1, JP H04 63810 A; and FR2699540 A1. However, such terpolymers including e.g. maleic anhydride, typically show unfavourable high water absorption and often exhibit significant yellowing. As a consequence, such terpolymers are often not suitable for high standard optical applications, in particular at elevated temperatures of up to 100 °C.

Another approach to obtain copolymers of olefinic monomers, such as ethylene or norbornene, and alkyl (meth) acrylate monomers, such as methyl acrylate and methyl methacrylate, is directed to coordination polymerisation (or also called insertion polymerisation) using transition metal complex catalysts, in particular based on palladium (e.g. KR 2021/0019282 A). The publication TANAKA RYO ET AL: "Synthesis of high-molecular weight block copolymers of norbornene and propylene with methyl methacrylate initiated by a fluorenylamido titanium complex", POLYMER CHEMISTRY, vol. 4, no. 14, (2013-01-01), pages 3974-3980, describes the preparation of norbornene, propylene, MMA copolymers via coordination-insertion polymerisation using a titanium complex.

Furthermore, it is known in the state of the art to produce alkyl (meth) acrylate/norbornene copolymers via metal-catalysed polymerisation. For example, the document US 2007/0255027 A1 is directed to a method of preparing alkene-acrylate-norbornene terpolymers via radical polymerisation under the presence of a Lewis acid, such as metal halides or metal oxides. As well, the document KR 2009/0020344 A is directed to radical polymerisation under the presence of a metal compound acting as Lewis acid. Said copolymer comprises 0.1 to 30 mol-% of a cyclic olefine monomer (such as norbornene), 10 to 99 mol-% of an acrylate-based monomer (such as methyl acrylate) and 0.1 to 50 mol of an unsaturated organic acid monomer (such as methacrylic acid). Use of metal catalyst leads to the need of a special filtering process to remove the catalyst that increases the production cost. Unwanted metal residuals in the polymer impair, for example, the weathering stability and often increase haze.

Generally, there is a high need to provide novel copolymers based on alkyl (meth) acrylate, in particular based on MMA, that exhibit improved heat resistance, C, high transparency and good processability, as well as limited moisture absorption and a low metal content.

Object of the present invention

Upon consideration of the above described shortcomings, it was an object of the present invention to provide a copolymer having excellent optical properties, in particular a low haze, in combination with high thermal stability e.g. Vicat temperature of at least 105 °C. These properties would allow use of the polymer with light sources having high operating temperatures on their surface, e.g. high-power white LEDs. Furthermore, the polymer needs to be suitable for a long-term use upon exposure to UV light

and/or increased temperatures and to have limited water absorption and an excellent weathering resistance, in particular, high stability against solar radiation.

- 5 A further goal of the present invention was provision of a method of manufacturing such copolymer on industrial scale in an cost and quality efficient manner. For example, the use of metal-based catalysts which need to be removed from the polymer product should be avoided.

Summary of the invention

- 10 It was surprisingly found that transparent copolymers of methyl methacrylate (MMA) and 2-norbornenen (NB) can be obtained via free radical polymerisation at reaction temperature above 100 °C, preferably above 120 °C, more preferably above 130 °C and wherein the starting monomer mixture or monomer feed comprises norbornene monomers in an amount of at least 20 mol-%, preferably at least 25 mol-%, based on the total amount of monomers in the starting monomer mixture. The inventive copolymer
15 obtained in the inventive process comprises at least 70.0 mol-% of MMA, 1.0 to 30 mol-% of NB and optional a selected co-monomer c), wherein the weight average molecular weight M_w of the copolymer is from 40,000 to 300,000 g/mol and wherein the sum of the repeating units derived from methyl methacrylate, NB and the optional co-monomer c) is at least 95.0 mol-%, preferably at least 98.0 mol-%.
- 20 A further aspect of the present invention relates to process for producing the inventive copolymer comprising radically copolymerisation of a monomer mixture, comprising MMA, a norbornene compound of formula (I), and, optionally, at least one co-monomer c) and/or d), to form the inventive copolymer, typically in form of a copolymer solution, copolymer dispersion or copolymer suspension, wherein the reaction temperature in copolymerisation step (a) is above 100 °C and the monomer mixture comprises at
25 least 10 mol-% of the norbornene compound of formula (I).

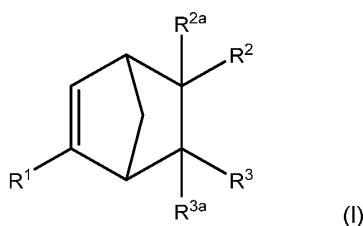
- A further aspect of the present invention relates to a moulding composition comprising the inventive copolymer and, optionally, one or more commonly known polymer additives. Particularly, the inventive moulding composition exhibit an excellent high thermal stability and a low haze. In particular, the Vicat
30 temperature (according to ISO 306-B50 (2014)) of the inventive moulding composition is at least 105°C and the haze (according to ASTM D1003 (2013), 3.0 mm) of the moulding composition is normally lower than 3 % when the moulding composition does not comprise colorants of scattering agents.

Detailed description of the invention

- 35 The present invention is directed to a copolymer comprising (all amounts given in mol.-% are based on the total copolymer):

- 40 a) from 70.0 to 99.0 mol-%, preferably from 75.0 to 99.0 mol-%, more preferably 80.0 to 98.5 mol-%, of repeating units derived from methyl methacrylate;

- b) from 1.0 to 30.0 mol-%, preferably from 1.0 to 25.0 mol-%, more preferably 1.5 to 20.0 mol-%, of repeating units derived from the compound represented by formula (I)



wherein the substituents R^1 , R^2 , R^{2a} , R^3 and R^{3a} are independently represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms; a hydroxy group (-OH); a hydroxy alkyl group; a carboxylic group (-C(O)OH); -C(=O)-NH₂; -C(=O)-R^x; -C(=O)-O-R^x; with R^x is C1-12-alkyl or C6-12-cycloalkyl; or R^2 and R^3 can build together a cyclic moiety; and

- c) from 0.0 to 15.0 mol-%, preferably from 0.0 to 10.0 mol-%, of repeating units derived from at least one optional co-monomer c) selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate;

wherein the weight average molecular weight M_w of the copolymer, determined by GPC, is from 40,000 to 300,000 g/mol, preferably from 50,000 to 200,000 g/mol;

and wherein the sum of a) the repeating units derived from methyl methacrylate, b) repeating units derived from the compound represented by the formula (I) and c) repeating units derived from optional co-monomer c) is at least 95.0 mol-%, preferably at least 98.0 mol-%, based on the total copolymer.

The term “(meth)acrylate” as used herein refers to methacrylates, e.g. methyl methacrylate, ethyl methacrylate, etc., as well as acrylates, e.g. methyl acrylate, ethyl acrylate etc. and also to mixtures thereof. The term “alkyl(meth)acrylates” as used herein may stand for a single alkyl (meth) acrylate or a mixture of different alkyl (meth) acrylates.

Preferably, the inventive copolymer is obtained by free radical polymerisation. In accordance with the present invention the term “free radical polymerisation” or corresponding terms, such as “free radically polymerised”, is understood as a chain polymerisation reaction wherein the chain initiation involves the dissociation of a radical polymerisation initiator molecule, such as usually known organic initiators selected from organic peroxides and azo compounds, effected by heat and/or light into free radicals. In particular, the free radical polymerisation exclude the use of any metal catalyst or metal compound which is directly involved in the polymerisation. The term “free radical polymerisation” is commonly known to a

skilled person and typically includes that the concentration of radicals is not constant during the polymerisation and that chain termination takes place, especially increased at high conversion rate. Therefore, the free radical polymerisation differs from commonly known controlled free radical polymerisation. Further, the free radical polymerisation as being a chain polymerisation reaction differs
5 from coordination polymerisation (or also called insertion polymerisation) typically using transition metal complex catalysts.

According to a preferred embodiment, the inventive copolymer is obtained by free radical polymerisation, preferably without using any metal or metal compound as initiator and/or catalyst.
10 Preferably, the inventive copolymer comprises less than 50 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, even more preferably less than 3 ppm, metals or metal compounds, calculated as metal, based on the total copolymer, and relating to metals selected from transition metals and aluminium (Al), more preferably relating to one or all of the metals selected from aluminium (Al), iron (Fe) and nickel (Ni). The amounts given above may refer to the amount of one specific metal or metal
15 compound or to the sum of all metals and metal compounds, present in the inventive copolymer.

Preferably, the inventive copolymer is a statistical or random copolymer. Typically, in a statistical copolymer the sequences of the repeating units along the copolymer chain follows statistical rules. Typically, in a random copolymer the molar ratio of repeating units in a particular section in the chain is
20 equal to the molar ratio of repeating unit in the whole copolymer. In this context, the structure of the inventive copolymer is typically not a block copolymer, an alternating copolymer or an graft copolymer.

Also preferably, the inventive copolymer comprises less than 50 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, even more preferably less than 3 ppm, metals or metal compounds,
25 calculated as metal, based on the total copolymer, and relating to the sum of all metals present in the inventive copolymer. More preferably, the inventive copolymer is free of any transition metals, aluminium and compounds thereof. Generally, according to the present invention the term "free of" or any corresponding term is understood in such way that the compound(s) mentioned is/are not present or is/are present at a level below the detection limit, referring to commonly known polymer analytic technics,
30 such as atomic absorption spectroscopy (AAS), typically after digestion; NMR techniques; wet chemistry analytics (e.g. titration methods).

The term "ppm" as used herein refers to means weight ppm (e.g. mg/kg), if not stated otherwise.

35 In a preferred embodiment the sum of a) the repeating units derived from a) methyl methacrylate, b) repeating units derived from the compound represented by the formula (I) and c) repeating units derived from optional co-monomer c) is at least 99.0 mol-%, more preferably at least 99.9 mol-%, based on the total copolymer. Also preferably, the copolymer is built up exclusively by the repeating units derived from a) methyl methacrylate, b) repeating units derived from the compound represented by the formula (I) and
40 c) repeating units derived from optional co-monomer c). Also preferably, the copolymer is built up

exclusively by the repeating units derived from a) methyl methacrylate, b) repeating units derived from the compound represented by the formula (I) and optionally c) repeating units derived from co-monomer c) selected from alkyl acrylates, such as methyl acrylate und ethyl acrylate. The term "is built up exclusively" means that the sum of the repeating units mentioned is 100.0 mol-%, based on the total amount of monomer repeating units in the copolymer. As a skilled person knows, such copolymer may comprise minor amount of groups resulting from the radical polymerisation initiator molecule and/or of chain transfer agent.

According to a preferred embodiment, in the inventive copolymer the content of repeating units derived from the compound represented by formula (I) p_b , in mol-%, in the copolymer, is described by the following relationship:

$$0.01 * p_a \leq p_b \leq 0.4 * p_a$$

more preferably by the following relationship:

$$0.04 * p_a \leq p_b \leq 0.3 * p_a$$

wherein p_a is the content of repeating units derived from methyl methacrylate, in mol-%, in the copolymer.

Preferably, the inventive copolymer has a Vicat softening temperature according to ISO 306-B50 (2014) of at least 105°C, preferably of at least 110°C, more preferably of at least 115 °C. More preferably the inventive copolymer has a Vicat softening temperature in the range of 105 °C to 135 °C more preferably in the range of 110 °C to 130 °C.

In particular, the haze of the inventive copolymer is lower than 3.0%, preferably lower than 2.0%, more preferably lower than 1.5%, wherein the haze is measured at 23 °C on an injection moulded specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to standard ASTM D1003 (2013). Also preferably, the haze of the copolymer is in the range of 0.01 to 2.9 %, particularly preferably in the range of 0.1 to 1.4 %.

Furthermore, light transmittance T_{D65} of the inventive copolymer is in the range of 85 to 93 %, more preferably in the range of 87 to 92.5 %, measured at 23 °C on an injection moulded specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to DIN 5033 - 7 (2014).

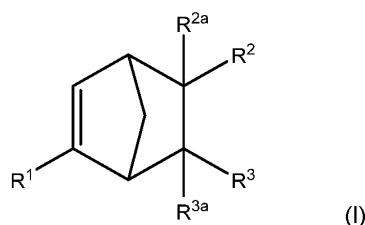
In a particular preferred embodiment the inventive copolymer comprises less than 50 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, even more preferably less than 3 ppm, metals or metal compounds, calculated as metal, based on the total copolymer, and relating to the sum of all metals present in the copolymer; wherein the haze of the inventive copolymer is lower than 3.0%, preferably lower than 2.0%, more preferably lower than 1.5%, wherein the haze is measured at 23 °C on an injection moulded specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to standard ASTM D1003 (2013); and wherein the light transmittance T_{D65} of the inventive copolymer is in the range of 85 to 93 %, more preferably in the range of 87 to 92.5 %, measured at 23 °C on an injection

moulded specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to DIN 5033 - 7 (2014).

It was surprisingly found, that the low amount of ,metal ions improves the transparency and transmittance of the copolymer.

Compound of formula (I) (monomer b))

The copolymer of the present invention comprises from 1.0 to 30.0 mol-%, preferably from 1.0 to 25.0 mol-%, more preferably from 1.5 to 20.0 mol-%, even more preferably from 1.5 to 15.0 mol-%, of repeating units derived from the compound represented by formula (I)

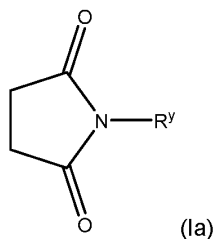


The substituents R^1 , R^2 , R^{2a} , R^3 and R^{3a} are independently represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms; a hydroxy group (-OH); a hydroxy alkyl group; a carboxylic group (-C(O)OH); -C(=O)-NH₂; -C(=O)-R^x; -C(=O)-O-R^x; with R^x is C1-12-alkyl or C6-12-cycloalkyl; or R^2 and R^3 can build together a cyclic moiety.

According to a preferred embodiment, the substituent R^1 is represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms. More preferably, the substituent R^1 is represented by a hydrogen atom or a C1-C4 alkyl group. Most preferably, the substituent R^1 is represented by a hydrogen atom or methyl. Even more preferably, the substituent R^1 is represented by a hydrogen atom.

For example, R^2 and R^3 can build together a cyclic moiety, wherein the cyclic moiety is preferably a 5 to 7 membered ring (including the carbon atoms of the norbornene structure), preferably including one or more heteroatoms selected from N and O. Preferably, the cyclic moiety is

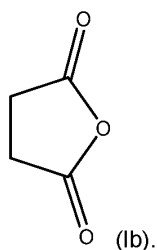
i) a dicarboxylic imide structure, represented by formula (Ia)



with R^Y is represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms, a hydroxy group (-OH), or a hydroxy alkyl group; or

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ii) a dicarboxylic anhydride structure, represented by formula (Ib)



Typically, a hydroxy alkyl group is a linear or branched C1-C12 alkyl group substituted with one or more, preferably one or two, hydroxy groups, provided that if two or more hydroxy groups are present they are not two or more hydroxy groups on the same carbon atom. Preferably, the hydroxy alkyl group is represented by $-R^X-OH$, with R^X is as defined above. Examples of hydroxy alkyl group are hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-(hydroxymethyl)-2-methylpropyl, 2-hydroxybutyl, 3-hydroxybutyl, 4-hydroxybutyl, 2,3-dihydroxypropyl, 1-(hydroxymethyl)-2-hydroxyethyl, 2,3-dihydroxybutyl, 3,4-dihydroxybutyl and 2-(hydroxymethyl)-3-hydroxypropyl.

The term "hydrocarbon group" as used in the present application encompasses alkyl, cycloalkyl, aryl, aralkyl, alkylaryl groups. These groups may be branched or unbranched. In addition, these groups may have one or several substituents. Substituents are, for example, linear and branched alkyl groups having 1 to 12, preferably 1 to 6 carbon atoms, for example methyl, ethyl, propyl, butyl, pentyl, 2-methylbutyl, hexyl, or 2-ethylhexyl; cycloalkyl groups, for example cyclopentyl and cyclohexyl; aromatic groups such as phenyl or naphthyl.

Preferred alkyl groups include methyl, ethyl, propyl, isopropyl, 1-butyl, 2-butyl, 2-methylpropyl, tert-butyl, iso-butyl, pentyl, 2-methylbutyl, 1,1-dimethylpropyl, hexyl, heptyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-decyl, 2-decyl, undecyl and dodecyl group. Preferred cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the cyclooctyl group, each of which may be optionally substituted with one or several branched or unbranched alkyl groups. Aromatic groups preferred in accordance with

the invention may derive from phenyl, naphthyl and biphenyl, each of which may also optionally be substituted with one or several branched or unbranched alkyl groups.

Each of the substituents R^2 , R^{2a} , R^3 and R^{3a} can be independently *exo*- or *endo*-configured. In case that
5 R^{2a} and R^{3a} are hydrogen, the substituents R^2 and R^3 may also be *cis*- or *trans*-configured in respect to each other.

For example, the compound of formula (I) is one or more compound selected from 2-norbornene (2-NB);
5-norbornene-2,3-dicarboxylic anhydride; 3-methyl-5-norbornene-2,3-dicarboxylic anhydride; 5-methyl-5-
10 norbornene-2,3-dicarboxylic anhydride; 2-carboxylic acid-5-norbornene; 2,3-dicarboxylic acid-5-norbornene; 2(2-hydroxyethyl)-2-carboxylic acid-5-norbornene; 2(2-hydroxyethyl)-3-carboxylic acid-5-norbornene; 2-carboxylic acid-2-tert butyl-5-norbornene; 2-carboxylic acid-3-tert butyl-5-norbornene; 2,3-dimethyl-2,3-dicarboxylic acid-5-norbornene; 5-norbornene-2-ol; 5-norbornene-2,2-dimethanol; 5-norbornene-2,3-dimethanol; 2-acetyl-5-norbornene; 5-norbornene-2-carboxylic methyl ester; 2-carboxylate-2-ethyl-5-norbornene; 2-carboxylate-3-ethyl-5-norbornene; 5-norbornene-2-carboxamide; *N*-(2-ethylhexyl)-5-norbornene-2,3-dicarboxylic imide; and *N*-hydroxy-5-norbornene-2,3-dicarboxylic imide.
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According to a preferred embodiment the compound represented by Formula (I) (monomer b)) is 2-norbornene (2-NB). In particular, use of 2-NB showed to deliver copolymers with excellent optical
20 properties and high thermal stability.

Optional co-monomer c)

In addition to repeating units derived from MMA, and the compound of formula (I) the copolymer of the
25 present invention may comprise (in each case based on the total copolymer) from 0.0 to 15.0 mol-%, preferably from 0.0 to 10.0 mol-%, more preferably from 0.0 to 7.0 mol-% of repeating units derived from at least one optional co-monomer c) which is selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate. Preferably, the copolymer may comprise repeating units derived from at least one optional co-monomer c), preferably
30 selected from acrylic acid, methacrylic acid, methyl acrylate and ethyl acrylate, in an amount of 0.01 to 10.0 mol-%, more preferably 0.1 to 5.0 mol-%.

Preferably, the optional co-monomer c) is at least one monomer selected from methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate.
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For the purposes of the present invention, preference is given to C_1 - C_{18} -alkyl (meth)acrylates, advantageously C_1 - C_{10} -alkyl (meth)acrylates, in particular C_1 - C_4 -alkyl (meth)acrylates. Most preferred alkyl methacrylates, different from methyl methacrylate (MMA), encompass ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, isobutyl methacrylate, *tert*.-butyl
40 methacrylate, *n*-pentyl methacrylate, *n*-hexyl methacrylate, *n*-heptyl methacrylate, *n*-octyl methacrylate,

n-isooctyl methacrylate, and *n*-ethylhexyl methacrylate, *n*-nonyl methacrylate, *n*-decyl methacrylate, and also cycloalkyl methacrylates, for example cyclohexyl methacrylate, isobornyl methacrylate or ethylcyclohexyl methacrylate. Preferred alkylacrylates encompass methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, isobutyl acrylate, *tert*.-butyl acrylate, *n*-pentyl acrylate, 5 *n*-hexyl acrylate, *n*-heptyl acrylate, *n*-octyl acrylate, isooctyl acrylate, *n*-nonyl acrylate, *n*-decyl acrylate, and *n*-ethylhexyl acrylate, and also cycloalkyl acrylates, for example cyclohexyl acrylate, isobornyl acrylate or ethylcyclohexyl acrylate.

Examples of suitable aromatic vinyl monomers include styrene; mono- or polyalkylstyrenes such as *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, *o,p*-dimethylstyrene, *o*-ethylstyrene, *m*-ethylstyrene 10 and *p*-ethylstyrene; styrene derivatives containing functional groups such as methoxystyrene, ethoxystyrene, vinylbenzoic acid, methyl vinylbenzoate, vinylbenzyl acetate, hydroxystyrene, *o*-chlorostyrene, *p*-chlorostyrene and divinylbenzene; 3-phenylpropylene, 4-phenylbutene and α -methylstyrene. Among these, styrene is mostly preferred.

15 Use of an alkyl acrylate, methacrylic acid and acrylic acid as an optional comonomer c) leads to even a better flowability of the copolymer, wherein preferred alkyl acrylate are selected from methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, isobornyl acrylate, ethylhexyl acrylate. Furthermore, isobornyl methacrylate, norbornyl methacrylate, *tert*.-butyl methacrylate and α -methylstyrene can also be used 20 as an optional comonomer c). In terms of an optimal balance of optical properties and high thermal stability, the at least one optional co-monomer c) is preferably selected from methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate.

If an additional improvement of flowability and/or a particularly low water absorption of the inventive 25 copolymer is desired, styrene or methacrylates such as butyl methacrylate, ethylhexyl methacrylate or aliphatic methacrylates of fatty acid esters such as octylmethacrylate, dodecyl methacrylate, stearyl methacrylate, palmitic methacrylate and other aliphatic C₁₂-C₂₄ methacrylates can also be employed as an optional comonomer c).

30 According to a preferred embodiment, the inventive copolymer comprises one or two optional comonomers c) selected from methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate. Even more preferably, the inventive copolymer may comprise one optional comonomer c) selected from methacrylic acid and acrylic acid, as well as one optional comonomer c) selected from methyl acrylate and ethyl acrylate.

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Optional co-monomer d)

In addition to repeating units derived from MMA (monomer a), repeating units derived from compound of formula (I) (monomer b) and repeating units derived from optional comonomer c), the copolymer of the 40 present invention may comprise from 0.0 to 5.0 mol-%, preferably from 0.0 to 2.0 mol-%, more preferably

from 0.0 to 1.0 mol-%, based on the total copolymer, of repeating units derived from an additional optional co-monomer d), which is different to the monomers a), b) and c) and which is radically copolymerisable with methyl methacrylate (monomer a)) and/or the compound represented by the formula (I) (monomer b) and/or optional co-monomer c).

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For example, the optional co-monomer d) is one or more monomer selected from (meth)acrylonitrile, maleic anhydride (MAH), maleimide, methylmaleimide, *N*-phenylmaleimide and *N*-cyclohexylmaleimide.

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According to a preferred embodiment, the inventive copolymer is free of any repeating units derived from monomers selected from maleic anhydride (MAH), maleimide, methylmaleimide, *N*-phenylmaleimide and *N*-cyclohexylmaleimide.

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Furthermore, the optional co-monomer d) may be one or more monomer selected from crosslinking monomers, wherein the crosslinking monomers have two or more polymerizable double bonds in the molecule. The crosslinking monomer may be selected from bifunctional (meth)acrylates, tri- or multifunctional (meth)acrylates, and other known crosslinkers. For example, the crosslinking monomer may be selected from allyl (meth)acrylate; (meth)acrylic acid anhydride; 1,2-butanediol-di(meth)acrylate; ethylene glycol dimethyl(meth)acrylate; trimethylolpropane-tri(meth)acrylate; 1,12-dodecandiol-di(meth)acrylate and divinylbenzenes. For example, bifunctional (meth)acrylates are di-esters of (meth)acrylic acid and a poly-functional alcohol, e.g. di(meth)acrylate of propane diol, butane diol, hexane diol, octane diol, nonane diol, decane diol, eicosane diol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dodecaethylene glycol, tetradecaethylene glycol, propylene glycol, dipropyl glycol, tetradecapropylene glycol. For example, tri- or multi-functional (meth)acrylates are tri- or multi-esters of (meth)acrylic acid and a poly-functional alcohol, e.g. trimethylolpropane tri(meth)acrylates and pentaerythritol tetra (meth)acrylate. Suitable cross-linking monomers are for example describes in WO 02/20634 and EP 0 522 351. Typically, the optional monomer d) selected from at least crosslinking monomer as described above may be present in an amount from 0.001 to 1.0 mol-%, based on the total copolymer. Preferably, the amount of crosslinking monomers is adjusted so that the copolymer can be processed via any known thermoplastic method, e.g. extrusion and injection moulding.

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Preparation of the copolymer

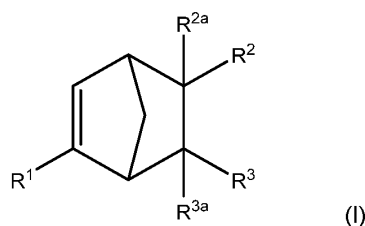
A further aspect of the present invention relates to a process for producing the inventive copolymer as described above comprising

35

- (a) a copolymerisation step, in which a monomer mixture, comprising MMA, a monomer of formula (I), and, optionally, at least one optional co-monomer c), undergoes radical copolymerisation to form the copolymer, typically in form of a copolymer solution, wherein the reaction temperature in copolymerisation step (a) is above 100 °C, preferably above 120 °C, more preferably above 130 °C and wherein the monomer mixture comprises at least 10 mol-

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%, preferably at least 20 mol-%, more preferably at least 30 mol-%, based on the total monomer mixture, of at least one monomer represented by formula (I)



wherein the substituents R^1 , R^2 , R^{2a} , R^3 and R^{3a} are independently represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms; a hydroxy group (-OH); a hydroxy alkyl group; a carboxylic group (-C(O)OH); -C(=O)-NH₂; -C(=O)-R^x; -C(=O)-O-R^x; with R^x is C1-12-alkyl or C6-12-cycloalkyl; or R^2 and R^3 can build together a cyclic moiety.

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The preferred embodiments of norbornene type monomer of formula (I) and of optional co-monomer c) as described above apply to the inventive process accordingly.

Copolymerisation step (a)

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Radical copolymerisation of monomer mixtures comprising MMA is per se well known in the prior art. The copolymerisation in step (a) can employ a method in which polymerisation is performed in a state containing said monomer mixture, a radical polymerisation initiator and, optionally, a chain transfer agent and not substantially containing a solvent (bulk polymerisation method). Alternatively, a solvent capable of dissolving the copolymer may be present or added during the polymerisation (solution polymerisation method).

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In a preferred embodiment the copolymerisation in step (a) is carried out via bulk polymerisation, in particular bulk polymerisation in terms of the present invention means that the monomer mixture comprises (preferably consist of) the monomers a), b), and optionally c) and/or d), a radical polymerisation initiator and, optionally, a chain transfer agent and not more than 5 wt.-%, preferably not more than 2 wt.-%, based on the total monomer mixture, of other components, such as solvent described below.

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According to a preferred embodiment, the process for producing the inventive copolymer comprises the copolymerisation step, in which a monomer mixture, comprising MMA, a monomer of formula (I), optionally, at least one optional co-monomer c), and at least one radical polymerisation initiator, selected from organic peroxides and azo compounds, undergoes radical copolymerisation to form the copolymer. Preferably, the reaction mixture is free of or only comprises a low amount as described below of transition metals and aluminium (Al), and compounds thereof, more preferably of metals selected from aluminium

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(Al), iron (Fe) and nickel (Ni), and compounds thereof. Also preferably, the reaction mixture comprises less than 100 ppm, preferably less than 50 ppm, more preferably less than 10 ppm, metals and metal compounds, based on the total amount of reaction mixture and based on the sum of all metals present in the reaction mixture. Also preferably, the reaction mixture comprises less than 200 ppm, preferably less than 100 ppm, more preferably less than 50 ppm, metals and metal compounds, based on the total amount of monomers in the reaction mixture, and based on the sum of all metals present in the reaction mixture.

For example, the radical polymerisation initiator can be one or more compound selected from organic peroxides and azo compounds. Preferably, the radical polymerisation initiator is at least one compound selected from organic peroxides. For example, suitable organic peroxides may be selected from tert.-butyl peroxy-3,5,5-trimethylhexanoate, tert.-butyl peroxy laurate, tert.-butyl peroxy isopropyl monocarbonate, tert.-hexyl peroxy isopropyl monocarbonate, tert.-butyl peroxy acetate, 1,1-bis(tert.-butyl peroxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert.-butyl peroxy)cyclohexane, tert.-butyl peroxy 2-ethylhexanoate (TBPEH), tert.-butyl peroxy isobutyrate, di-tert.-amylperoxid, didecanoyl-peroxide, tert.-amyl-peroxy-2-ethylhexylcarbonat, tert.-hexyl peroxy 2-ethylhexanoate, di-tert.-butyl peroxide, 2,5-dimethyl-2,5-bis(tert.-butyl peroxy) hexane, lauroyl peroxide, benzoyl peroxide, tert.-butyl peroxy neodecanoate, tert.-butyl peroxy pivalate, tert.-butyl peroxy-2-ethylhexanoate, tert.-butyl peroxy benzoate and dicumyl peroxide. For example, suitable azo compounds may be selected from 2-(carbamoylazo)-isobutyronitrile, 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), dimethyl 2,2'-azobisisobutyrate, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), 2,2'-azobis-4-methoxy-2,4-dimethylvaleronitrile and 2,2'-azobis-2,4-dimethylvaleronitrile.

Preferably, the reaction temperature in copolymerisation step (a) is in the range from 100 °C to 200 °C, preferably from 120 °C to 180 °C, more preferably from 130 °C to 180 °C. Preferably, the copolymerisation step (a) is carried out at a pressure in the range from 1 bar to 50 bar.

Preferably, the monomer mixture (e.g. the total monomer feed in a continuous or quasi-continuous polymerisation process) comprises from 10.0 to 70.0 mol-%, preferably from 20.0 to 60.0 mol-%, more preferably from 30.0 to 50.0 mol-%, based on the total amount of polymerizable components or preferably based on the total monomer mixture (e.g. in case of bulk polymerisation), of at least one monomer represented by formula (I), preferably of 2-norbornene.

In a preferred embodiment, the content of the compound represented by formula (I) (monomer b) m_b , in mol-%, in the total monomer mixture (e.g. in the total monomer feed of a continuous polymerisation process) in the copolymerisation step (a), is described by the following relationship:

$$0.2 * m_a \leq m_b \leq 2.0 * m_a$$

more preferably by the following relationship:

$$0.25 * m_a \leq m_b \leq 1.5 * m_a$$

wherein m_a is the content of the methyl methacrylate (monomer a), in mol-%, in the monomer mixture.

Preferably, the monomer mixture (e.g. the total monomer feed) in the copolymerisation step (a) comprises (preferably consists of), based on the total amount of polymerizable components or preferably based on the total monomer mixture:

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- a) from 30.0 to 90.0 mol-%, preferably 40.0 to 80.0 mol-%, more preferably 49.9 to 70.0 mol-%, of methyl methacrylate;
- b) from 10.0 to 70.0 mol-%, preferably 20.0 to 60 mol-%, more preferably 30.0 to 50.0 mol-%, of the compound represented by formula (I), more preferably 2-norbornene; and
- 10 c) from 0.0 to 15.0 mol-%, preferably 0.0 to 10 mol-%, more preferably 0.01 to 10 mol-%, of at least one optional co-monomer c) selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate; more preferably selected from methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate.

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For example, the monomer mixture (e.g. the total monomer feed) in the copolymerisation step (a) comprises (preferably consists of), based on the total amount of polymerizable components or preferably based on the total monomer mixture:

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- a) from 30.0 to 80.0 mol-%, preferably 49.9 to 75.0 mol-%, of methyl methacrylate;
- b) from 20.0 to 60.0 mol-%, preferably 25.0 to 50 mol-%, of the compound represented by formula (I), preferably 2-norbornene;
- c) from 0.0 to 10.0 mol-%, preferably 0.1 to 8 mol-%, of at least optional co-monomer c) selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate; preferably selected from
- 25 methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate; and
- d) from 0.0 to 5.0 mol-%, preferably from 0.0 to 1.0 mol-%, of at least one optional co-monomer d).

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Typically, the conversion in the copolymerisation step (a) is at least 40%, preferably at least 45%. The term "conversion" as used in the present application refers to an average weight ratio of the copolymer formed in the copolymerisation step (a) to the total monomer feed.

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Preferably, the reaction time or the total average residence time (in case of a continuous polymerisation process) of the copolymerisation step (a) is in the range of from 10 minutes to 10 hours, more preferably from 15 minutes to 6 hours, for instance from 20 minutes to 4 hours.

Typically, in case of a batch polymerisation the reaction time of the copolymerisation step (a) can be in the range of 1 to 30 hours, preferably 4 to 24 hours.

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The copolymerisation step (a) can be carried out in a discontinuous reactor (batch) or a semi-batch reactor type, in which radical polymerisation initiator, monomer, and if present, solvent or a combination of any of those is optionally fed during the copolymerisation step (a). Alternatively, the copolymerisation step (a) can be performed in a continuous polymerisation process like in stirred tank reactors (CSTR), in a tubular reactor or a combination thereof, in kneaders or in disc ring reactors.

In some embodiments, the polymer reaction mixture from outlet of the first CSTR can be successively continuously supplied to a second and/or third reaction device, as an example a further CSTR or to a tubular reactor in order to increase the conversion.

A discontinuous reactor (batch), semi-batch reactor and the CSTR can be equipped with any kind of mixing elements to homogenize the reaction mixture in the reactor. These reactors are also called back-mixed in the literature (Octave Levenspiel, Chemical Reaction Engineering 3rd ed Wiley 1998). In a further embodiment, the discontinuous reactor (batch) contains no mixing elements. The copolymerisation step may further take place in cast sheet.

The design of the discontinuous reactor (batch), semi-batch reactor and CSTR is not particularly limited. Typical examples thereof are vessels with installed stirrers where the stirrer shaft is carrying the mixing elements like paddles, blades, anchor or helical mixing elements. The polymerisation vessel optionally contains a heated or cooled jacket with circulating hot oil, water or water steam to heat or cool the reaction mixture during polymerisation. A further effective way of heat removal is cooling of the reaction mixture by feeding the monomers and or the solvent having a lower temperature than the polymerisation temperature. Alternatively the polymerisation heat removal can be performed by boiling cooling of the reaction mixture.

The copolymerisation step (a) can also be carried out in a continuous tubular reactor. A continuous tubular reactor contains at least one inlet port for the monomer or pre-polymer reaction mixture and at least one outlet port for the polymer reaction mixture. The tubular reactor can also be a tubular bundle reactor where the polymerisation is performed for example in one or more parallel arranged tubes. An alternative tubular reactor can also be a plate heat exchanger. In contrast to a CSTR, a tubular reactor does not contain a well-mixed or homogenized reaction mixture over the whole reaction volume. A typical tubular reactor as it is defined in the literature (Octave Levenspiel, Chemical Reaction Engineering 3rd ed Wiley 1998) contains large scale concentration gradients between the inlet port area and the outlet port area. The tubular reactor may optionally contain static mixing elements or a stirrer to homogenize the reaction mixture in the radial direction. Examples of static mixing elements include SMX type and SMR type Sulzer tubular mixers, Kenics static mixers, Toray tubular mixer, etc. Alternatively, the tubular reactor may not contain any mixing elements. The polymerisation heat removal of the tubular reactor can optionally be performed by a jacket filled with water or hot oil. Alternatively the polymerisation heat removal can be done by boiling cooling of the reaction mixture.

The conversion rate can be readily adjusted by a skilled person by adapting the average residence time of the reaction mixture in the reactor, polymerisation temperature, reactivity of the radical polymerisation initiator used and the amount of the initiator, as well as monomer concentration in the reactor feed. For instance, if a CSTR is used, the average residence time is preferably selected in range from 10 minutes to 10 hours, more preferably from 15 minutes to 6 hours, for instance from 20 minutes to 4 hours. If the average residence time is shorter than 20 minutes, it becomes necessary to increase the amount of the radical polymerisation initiator, making it difficult to control the polymerisation reaction. Average residence times above 7 hours are generally disadvantageous in terms of productivity and cost-efficiency.

- 10 The polymerisation vessel used as a CSTR in the step (a) is not particularly limited, as long as the reaction mixture during the copolymerisation step (a) is sufficiently mixed.

In one embodiment of the present invention, the copolymerisation step (a) is carried out in a Continuous Stirred Tank Reactor (CSTR) and the composition and temperature of the reaction mixture can be kept substantially homogenous by means of a suitable stirrer installed in the polymerisation vessel. A CSTR type reactor equipped with a stirrer, in which said stirrer has stirring blades capable of keeping the solution in the vessel substantially completely mixed, is normally used.

The shapes of the stirring blades can be those of publicly known stirring blades. For example, double helical blades, paddle blades, turbine blades, propeller blades, Brumagin blades, multi-stage blades, anchor blades, max blend blades, puddle blades, MIG blades, the full-zone blades and Logborn blades produced by Kobelco Eco-Solutions Co., Ltd. and the like can be used for this purpose. Above all, double helical ribbon blades are particularly preferred due to their high stirring efficiency. Furthermore, to enhance the stirring effect, it is preferred to install baffles in the polymerisation vessel.

If a solution polymerisation method is employed, the solvent used in the step (a) is not especially limited as long as it is capable of dissolving the copolymer at the polymerisation temperature as described before and does not interfere with the polymerisation process except some minor chain transfer. One or more solvents selected from aromatic hydrocarbons, ketones, ethers, esters, amides and alcohols can be used. Examples of a solvent that can be used include but are not limited to publicly known organic solvents such as toluene, xylene, 2,5-dimethylfuran, acetone, methyl ethyl ketone, methyl-*n*-butyl ketone, methyl isobutyl ketone, ethyl isobutyl ketone, tetrahydrofuran, dioxane, butyl acetate, ethyl acetate, dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide, *N*-methyl pyrrolidone, methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, 2-methoxy-2-propanol and tetraglyme, or a mixture of any of those. If the copolymerisation step (a) is performed in a solvent, the solvent content in the reaction mixture typically ranges between 3.0 wt.-% and 60 wt.-%, more preferably between 5.0 wt.-% and 45 wt.-%, based on the total weight of the reaction mixture.

Preferably, the copolymerisation step (a) is carried out as bulk polymerisation or in presence of a solvent which is preferably selected from toluene, xylene, butyl acetate, ethyl acetate, dimethylfurane, methyl ethyl ketone or a mixture of any of those, preferably as bulk polymerisation.

5 Heating step (b)

According to the present invention, the copolymer solution obtained in the polymerisation step (a) can be optionally continuously supplied to a step of heating the copolymer solution to a temperature from 100 °C to 300 °C (heating step (b)). Typically, the optional heating step may be carried out in commonly known
10 heat exchanging device.

Devolatilization step (c)

Subsequently, the material can be supplied to a devolatilization apparatus in the subsequent
15 devolatilization step, to separate and remove the unreacted monomers or the mixture consisting of the unreacted monomers and, if present, the solvent (devolatilization step (c)).

The temperature of the copolymer solution or the melt temperature of the copolymer in the devolatilization step is typically lower than 300 °C, more preferably from 150 °C to 300 °C, even more preferably from
20 170 °C to 280 °C. The preferred pressure in the last devolatilization zone of the devolatilization step is an absolute pressure, typically below 950 mbar, preferably below 500 mbar, more preferably below 200 mbar. The lower limit of the absolute pressure in the devolatilization step is not limited, but for technical reasons it is normally at least 10 mbar or higher. If the pressure in the devolatilization step is higher than 500 mbar, even if devolatilization is performed in said temperature range, the unreactive monomers or the
25 mixture consisting of the unreactive monomers and the polymerisation solvent cannot be separated or removed efficiently. This is disadvantageous in terms thermal stability, mechanical and optical properties of the resulting copolymer.

As an apparatus for performing such devolatilization, a single screw or a twin-screw extruder, a flash
30 chamber, a degassing kneader or a combination thereof can be used. One embodiment is an apparatus that has a cylindrical container and a stirrer having multiple stirring elements attached to a rotating shaft, and has at least one or more vent holes at the top of the cylindrical portion, a supply port for supplying the copolymer solution at one end of the cylindrical portion and a discharge port for taking out the copolymer after completion of devolatilization at the other end may be used. The number of rotating shafts is not
35 limited but is usually 1 to 5, preferably 1 or 2, and an apparatus having two rotating shafts is more preferred. Particularly, a vented continuous single or twin screw extruder (kneading apparatus and batch type melt kneading apparatus) are preferred, and a single screw extruder, double screw extruder, double screw/single screw combined continuous kneading extruder and triple screw extruder respectively with "Unimelt" type screw(s), and continuous or batch type kneading machine can be mentioned here. Above

all, especially a vented single or double screw extruder or a continuous double screw reactor with multiple convex lens type and/or elliptical plate paddles can be preferably used.

Further, the devolatilization step in the production process of this invention can employ a method of using
5 two or more devolatilization apparatuses disposed in series, to perform the devolatilization, and this is advantageous since the remaining volatile component in the copolymer obtained after devolatilization can be decreased even further.

The degassed unreacted monomers and solvent can optionally be recycled and used in the
10 copolymerisation step (a) again, optionally alone or together with virgin monomer and optionally virgin solvent.

Moulding composition

15 A further aspect of the present invention relates to a moulding composition comprising the copolymer of the present invention and, optionally, at least one additive selected from UV absorbers, UV stabilizers, antioxidants, colourants, flow improvers, anti-static agents, lubricants and demoulding aids, scattering particles, scratch improving aids etc.

20 The preferred embodiments and ranges defined for the inventive copolymer applies to the inventive moulding composition accordingly. In particular, the amount of metals or metal compounds, preferably of transition metals and aluminium (Al), more preferably of metals selected from aluminium (Al), iron (Fe) and nickel (Ni), as defined above for the inventive copolymer applies to the inventive moulding composition as well.

25 Particularly, the inventive moulding composition exhibit an excellent high thermal stability. Preferably, the Vicat softening temperature of the inventive moulding composition, measured according to ISO 306-B50 (2014), is at least 105°C, more preferably at least 110 °C, even more preferably 115 °C, also preferably in the range of 105 to 135 °C, also preferably in the range of 110 to 130 °C.

30 The inventive moulding composition of the present invention has an excellent transparency and a clear, substantially non-cloudy appearance. In particular, haze of the moulding composition, preferably in the case that the moulding composition does not comprise colour additives, colouring pigments or scattering agents, is lower than 5.0%, preferably lower than 4.0%, more preferably lower than 3.0%, even more preferably lower than 1.0 %, wherein the haze is measured at 23 °C on an injection moulded specimen having a thickness of 3.0 mm according to standard ASTM D1003 (2013). Also preferably, the haze of the moulding composition is in the range of 0.01 to 2.9 %, particularly preferably in the range of 0.1 to 1.4 %.

Furthermore, the inventive moulding composition, preferably in the case that the moulding composition
40 does not comprise colour additives, colouring pigments or scattering agents, preferably shows a light

transmittance T_{D65} in the range of 85 to 93 %, more preferably in the range of 87 to 92.5 %, measured at 23 °C on an injection moulded specimen having a thickness of 3.0 mm according to DIN 5033 - 7 (2014).

5 It was further found, that moulded articles, such as light-guide bodies, having higher thickness as well as excellent transparency, can be prepared by the inventive copolymer. In this context, the inventive moulding composition shows a light transmittance T_{D65} in the range of 75 % to 93 %, more preferably in the range of 80.0 to 92.5 %, measured at 23 °C on an injection moulded specimen having a thickness of 150.0 mm according to DIN 5033 - 7 (2014).

10 The yellowness index of the inventive moulding composition, preferably in the case that the moulding composition does not comprise colour additives, colouring pigments or scattering agents, should preferably be less than 5, preferably less than 3, more preferably less than 2, measured at 23 °C on an injection moulded specimen having a thickness of 3.0 mm, according to DIN 6167 (1980) (illuminant D_{65} , 10° on 3.0 mm layer thickness).

15 The yellowness index of the inventive moulding composition, preferably in the case that the moulding composition does not comprise colour additives, colouring pigments or scattering agents, should preferably be less than 12, preferably less than 8, measured at 23 °C on an injection moulded specimen having a thickness of 150.0 mm, according to DIN 6167 (1980) (illuminant D_{65} , 10° on 3.0 mm layer
20 thickness).

Particularly, the ranges given above regarding haze, transmission and/or yellowness index apply to moulding composition that does not comprise any colorants and/or scattering agents. In particular, such scattering agents also includes unwanted impurities, such as metal salts and agglomerated metal salts.

25 Due to its advantageous rheological properties, such as melt volume flow rate MVR measured according to ISO 1133 (2012), the moulding composition of the present invention is highly suitable for the manufacturing of optical elements by means of injection moulding.

30 The moulding composition may contain at least one common polymer additive as long as the later do not adversely affect optical properties of the copolymer of the present invention. Various polymer additives are well known to a skilled person and include inter alia UV absorbers, UV stabilizers, light stabilizers, antioxidants, colourants, flow improvers, flame retardants, lubricants and de-moulding aids, scattering particles etc. Thermal stability of the resulting moulding composition should not be excessively impaired
35 by these additives.

UV absorbers and UV stabilizers and light stabilizers for use in the present invention are well known and described in detail by way of example in Hans Zweifel, Plastics Additives Handbook, Hanser Verlag, 5th Edition, 2001, p. 141 ff. UV stabilizers are understood to include UV stabilizers and free-radical
40 scavengers. Free radical scavengers are for example sterically hindered phenols like, without restrictions,

octadecyl-3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate], pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate]. UV absorbers can e.g. derive from the group of the substituted benzophenones, salicylic esters, cinnamic esters, oxanilides, benzoxazinones, hydroxyphenylbenzotriazoles, benzotriazoles, triazines or benzylidenemalonate. The total content of the UV absorbers in the moulding composition typically ranges from 0.01 wt.-% to 1.0 wt.-%, especially from 0.01 wt.-% to 0.5 wt.-%, in particular from 0.02 wt.-% to 0.2 wt.-%, based on the weight of the moulding composition.

The UV absorbers may be present in the moulding composition as low molecular weight compounds. However, UV-absorbing groups in the matrix polymer molecules may also be covalently bonded after copolymerisation with polymerisable UV-absorbing compounds, such as, for example, acrylic, methacrylic or allyl derivatives of benzophenone derivatives or benzotriazole derivatives. As will be readily appreciated by a skilled person, mixtures of chemically different UV absorbers may also be employed, e.g. benzotriazoles in combination with triazines.

The best-known representatives of the UV stabilizers/free-radical scavengers are provided by the group of hydroxyphenyl benzotriazole or sterically hindered amines (hindered amine light stabilizer, HALS). Examples of suitable free radical scavengers/UV stabilisers include *inter alia* sterically hindered phenols and sterically hindered amines, which are known by the name HALS ((Hindered Amine Light Stabiliser). The tetramethylpiperidine group present in the HALS compounds is responsible for the stabilising effect thereof. This class of compounds may be either unsubstituted or substituted by alkyl or acyl groups on the piperidine nitrogen. The sterically hindered amines do not absorb in the UV range. Examples of hydroxyphenyl benzotriazole are 2-(2H-benzotriazol-2-yl)-p-cresol, sold as Tinuvin® P or Drometrizole. They trap free radicals formed, which once again the UV absorbers are incapable of doing. The free radical scavengers / UV stabilisers are used in the compositions according to the invention in amounts of 0.01 wt.-% to 1.5 wt.-%, especially in amounts of 0.02 wt.-% to 1.0 wt.-%, in particular, in amounts of 0.02 wt.-% to 0.5 wt.-%, based on the weight of the moulding composition. Also a combination of UV stabilisers / absorbers, light stabilizers and antioxidants are possible.

Lubricants and mould release agents which can reduce or completely prevent possible adhesion of the moulding composition to the injection mould are important for the injection moulding process and may also be employed. For example, lubricants, selected from the group consisting of saturated fatty acids, esters or inorganic salts having less than C₂₀, preferably C₁₆ to C₁₈, carbon atoms or of the saturated fatty alcohols having less than C₂₀, preferably C₁₆ to C₁₈, carbon atoms, may be present as auxiliaries. For example, stearic acid, stearyl alcohol, palmitic acid, palmitic alcohol, lauric acid, lactic acid, glycerol monostearate, pentaerythritol, and industrial mixtures of stearic and palmitic acid. Also suitable are *n*-hexadecanol, *n*-octadecanol and industrial mixtures of *n*-hexadecanol and *n*-octadecanol and glycerol monostearate. A particularly preferred lubricant or mould release agent is stearyl alcohol. The lubricants are typically used in amounts of not more than 1.0 wt.-%, e.g. 0.05 wt.-% to 0.25 wt.-% based on the weight of the moulding composition.

Use of moulding composition and moulded article

5 The moulding composition of the present invention can be processed into a moulded article via any known common thermoplastic process, e.g. injection moulding or extrusion, under usual processing conditions. The injection moulding of the composition can be performed in a known manner at temperatures in the range of from 220 °C to 280 °C (melt temperature) and a mould temperature of preferably from 60 °C to 120 °C. The extrusion is preferably carried out at a temperature of from 220 °C to 280 °C.

10

Because of its high thermal stability and a low haze, the moulding composition and moulded article made thereof are highly suitable for optical applications such as lighting and glazing. Such applications include light guides, lenses and glazing, for example glass covers for motor vehicle lights, *i.e.* headlamps or rear lights; covers for automobile lights; further varied lighting applications for building interior and/or exterior lighting which have to meet high demands particularly with regard to vandalism, thermal stability and good processability.

15

The moulding composition of the invention can be further advantageously used in optical disk or lens, , display or lighting component for communication devices, especially PDAs, mobile phones, preferably smartphones; tablet PCs; TV devices; kitchen appliances and other electronic devices.

20

The present invention is directed to a moulded article produced from the inventive moulding composition. In particular, the present invention is directed to a moulded article produced from the inventive moulding composition as described above, wherein the moulded article is selected from display components (e.g. for communication devices, such as mobile phones, smartphones, tablet PCs, TV devices, kitchen appliances); lighting components (e.g. light guides or lamp covers, preferably for room lighting systems or automobile lighting equipment); components in the automotive exterior (e.g. light applications, sensor covering, design elements, black coloured pillar trims, covers for automobile lights); components in the automotive interior (e.g. light applications, sensor covering, design elements, instruments, covers for automobile lights); components for optoelectronic devices (e.g. components for light emitting diodes (LEDs)); components for optical sensors; components for solar cells; optical elements (e.g. optical lenses); and components for medical devices having a light source.

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The following examples illustrate the invention in a greater detail. However, there is no intention that the present invention be restricted to these examples.

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Examples

1. Preparation of copolymer A

1.1 Materials

The following starting materials were used:

- | | | |
|----|------|---|
| 10 | MMA | methyl methacrylate, purity of > 99.6% from Röhm GmbH, Darmstadt, Germany |
| | MA | methyl acrylate, purity > 99 % from Sigma Aldrich, St. Louis, United States |
| | 2-NB | 2-norbornene, purity of > 99.9% from VWR International Merck |
| | MAA | methacrylic acid, purity of > 99.6% from Röhm GmbH, Darmstadt, Germany |
| | DDM | <i>n</i> -dodecylmercaptane, purity of 98 % from Dr. Spiess Chemische Fabrik GmbH, Kleinkarlbach, |
| 15 | | Germany |
| | DTA | di-tert-amylperoxide, Luperox® DTA, from Sigma Aldrich, St. Louis, United States |

1.2 Copolymerisation process and preparation of moulding compositions

- 20 Examples 1-5 (inventive) and Example 6 (comparative) were carried out in a technical scale CSTR encompassing stirred stainless-steel vessel. The polymerisation was carried out at a pre-defined temperature and at a pressure of higher than 10 bar. The polymerisation conditions are summarized in Table 1 below.
- 25 *n*-Dodecylmercaptane (DDM) was used as a chain transfer agent and di-tert-amylperoxide (DTA) was employed as a radical polymerisation initiator. Compositions of the reactor feed are specified in Table 1 below. The amount of components, given in wt.-% and mol-% in table 1, are given based on the total molar amount of monomers.
- 30 In order to ensure a steady state operation, the reactors were operated for about 6 hours before material samples were taken.

Table 1. Reactor feed composition and polymerisation conditions for examples 1-6

Example	1	2	3	4	5	6*
Reactor feed						
MMA [wt.-%]	75.00	74.36	71.01	71.28	66.00	98.50
MMA [mol.-%]	73.83	73.17	69.45	69.79	64.29	98.26
2-NB [wt.-%]	25.00	25.64	25.00	25.64	29.00	0
2-NB [mol.-%]	26.15	26.81	25.97	26.68	30.00	0
MAA [wt.-%]	0	0	4.00	3.08	5.00	0
MAA [mol.-%]	0	0	4.55	3.51	5.66	0
MA [wt.-%]	0	0	0	0	0	1.5
MA [mol.-%]	0	0	0	0	0	1.74
DDM [wt.-%]**	0.11	0.21	0.16	0.16	0.09	0.36
DTA [wt.-%]**	0.09	0.30	0.07	0.29	0.08	0.04
Polymerisation conditions						
Residence time [min]	46	46	45	46	44	20
Reactor temperature [°C]	150	154	150	154	150	150
Conversion [%]	50	59	51	59	46	51

*comparative example

**based on the total molar amount of monomers

5

The continuous copolymer solution outlet of the CSTR was heated to 210 °C in a heat exchanger downstream of the reactor and then devolatilized and pelletized in a single screw extruder. Pellets of the copolymers were obtained.

10 2. Test results

The obtained pellets were injection moulded at 250 °C to 3 mm thick platelets for investigation of optical properties and Vicat softening temperature (VST) B50, °C according to ISO 306. For all other tests, the pellets were used directly.

15

Properties and composition of the obtained copolymers are summarized in Table 2 below. The composition of the copolymers were obtained via ¹H-NMR as described below.

The amounts of monomer units are given based on the total amount of copolymer in table 2.

Table 2: Composition and properties of copolymers for examples 1-6

Example	1	2	3	4	5	6*
Copolymer composition						
MMA [wt.-%]	95.50	93.80	90.70	91.00	89.00	99.00
MMA [mol-%]	95.13	93.43	89.67	90.04	87.96	98.84
2-NB [wt.-%]	4.60	6.20	3.70	6.40	6.10	0
2-NB [mol-%]	4.87	6.57	3.89	6.73	6.41	0
MA [wt.-%]						1.00
MA [mol-%]						1.16
MAA [wt.-%]	0	0	5.60	2.80	4.90	0
MAA [mol-%]	0	0	6.44	3.22	5.63	0
2-NB / MMA [mol/mol]	0.051	0.070	0.043	0.075	0.073	0
Copolymer properties						
Metal content [ppm]**	< 5	< 5	< 5	< 5	< 5	< 5
VST, B50 / [°C],	117.6	117.6	121.8	120.3	122.5	110.0
Y.I., 3 mm / [-]	0.54	0.94	0.64	1.51	0.64	0.39
T, D ₆₅ , 3 mm / [%]	92.33	92.09	92.09	91.94	91.78	92.30
Haze / [%]	0.27	0.48	0.22	0.49	0.46	0.38
M _w / [g/mol]	116,490	58,923	98,900	61,931	122,000	101,000
M _n / [g/mol]	60,687	32,730	51,400	36,070	56,800	50,200
D / [-]	1.92	1.80	1.93	1.72	2.15	2.01

*comparative example

**contents of Al, Fe or Ni

5

3. Test methods

GPC Measurement conditions

- 10 The molecular weights, Mw (weight average molecular weight) and Mn (number average molecular weight) as well as molecular weight distribution and dispersity D (Mw/Mn) were determined using gel permeation chromatography (GPC) with following test conditions

	Eluent:	THF (HPLC-Grade) + 0.2 vol.-% TFA
	Flow rate:	1 ml / min
	Injected volume:	100 µl
	Detection:	RI HPS
5	Concentration of sample solution:	2 g/l
	Standard:	PMMA

Product properties

- 10 3.0 mm thick specimens were prepared by injection moulding at 250 °C and subsequently stored for 72 h at 23 °C and relative humidity of 50 % before the measurements.

- Haze (in [%]) was determined using hazemeter BYK Gardner Hazegard-plus according to ASTM D 1003 (1997). Optical transmission (T in [%]) was measured using a Varian Cary 5000 spectrophotometer according to ISO 13468-2 (2006). Yellowness Index (Y.I.) was measured using a Varian Cary 5000 spectrophotometer according to DIN 6167 (1980) (illuminant D65, 10° on 3.0 mm layer thickness).
- 15

- Vicat softening temperature (VST in [°C]) was measured according to ISO 306-B50 (2014) using 3.0 mm thick specimens which were stored for 16 h at 105 °C before the measurements.

20

The melt flow rate (MVR in [ml/10 min]) was determined according to ISO 1133 (2011) at 230 °C under a load of 3.8 kg.

Copolymer composition

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Composition of the copolymers was determined using ¹H-NMR spectra, recorded on a 400 MHz NMR Spectrometer from Bruker.

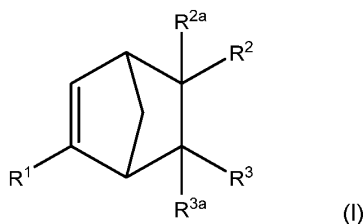
- Determination of MAA units in the copolymer were carried out by titration as described in WO 2022/122806 A1. The content of and glutaric anhydride units in the final copolymer was below 1 wt.-% and the amount was included in the value of MMA units.
- 30

- The contents of aluminium (Al), iron (Fe) and nickel (Ni) in the copolymers were determined via atomic absorption spectroscopy (AAS) after digestion of the copolymer. The content of each metal (Al, Fe, Ni) was below 5 µg/g (= 5ppm) (copolymer).
- 35

Claims

1. A copolymer comprising

- 5 a) from 70.0 to 99.0 mol-% of repeating units derived from methyl methacrylate;
 b) from 1.0 to 30.0 mol-% of repeating units derived from the compound represented by formula (I)



10 wherein the substituents R¹, R², R²ᵃ, R³ and R³ᵃ are independently represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms; a hydroxy group; a hydroxy alkyl group; a carboxylic group; -C(=O)-NH₂; -C(=O)-Rˣ; -C(=O)-O-Rˣ; with Rˣ is C1-12-alkyl or C6-12-cycloalkyl; or R² and R³ can build together a cyclic moiety; and

15 c) from 0.0 to 15.0 mol-% of repeating units derived from at least one optional co-monomer
 c) selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate;

20 wherein the weight average molecular weight M_w of the copolymer, determined by GPC, is from 40,000 to 300,000 g/mol, preferably from 50,000 to 200,000 g/mol;

and wherein the sum of the repeating units derived from methyl methacrylate, the compound represented by the formula (I) and the optional co-monomer c) is at least 95.0 mol-%, preferably at least 98.0 mol-%, based on the total copolymer.

25

2. Copolymer according to Claim 1, wherein the copolymer is obtained by free radical polymerisation.

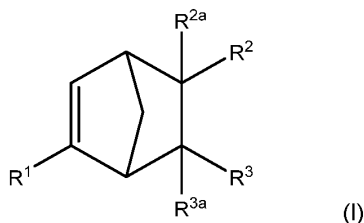
3. Copolymer according to Claim 1 or 2, wherein the copolymer comprises less than 50 ppm, preferably less than 10 ppm, metals or metal compounds, calculated as metal, based on the total copolymer, and relating to metals selected from transition metals and aluminium.

30

4. Copolymer according to any of Claims 1 to 3, wherein the copolymer comprises less than 50 ppm, preferably less than 10 ppm, metals or metal compounds, calculated as metal, based on the total copolymer, and relating to the sum of all metals present in the inventive copolymer.

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5. Copolymer according to any of Claims 1 to 4, wherein the inventive copolymer comprises less than 50 ppm, preferably less than 10 ppm, metals or metal compounds, calculated as metal, based on the total copolymer, and relating to the sum of all metals present in the copolymer;
 5 wherein the haze of the inventive copolymer is lower than 5.0%, preferably lower than 3.0%, wherein the haze is measured at 23 °C on an injection moulded specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to standard ASTM D1003 (2013); and wherein the light transmittance T_{D65} of the inventive copolymer is in the range of 85 to 93 %, more preferably in the range of 87 to 92.5 %, measured at 23 °C on an injection moulded
 10 specimen prepared from the inventive copolymer having a thickness of 3.0 mm according to DIN 5033 - 7 (2014).
6. Copolymer according to any of Claims 1 to 5, wherein the compound represented by Formula (I) is 2-norbornene.
- 15 7. Copolymer according to any of Claims 1 to 6, wherein the optional co-monomer c) is at least one monomer selected from methacrylic acid, acrylic acid, methyl acrylate and ethyl acrylate.
8. Copolymer according to any of Claims 1 to 7, wherein the copolymer has a Vicat softening
 20 temperature according to ISO 306-B50 (2014) of at least 105°C , preferably of at least 110°C.
9. Copolymer according to any of Claims 1 to 8, wherein the copolymer is a statistical or random copolymer.
- 25 10. A process for producing a copolymer according to any of Claims 1 to 9 comprising
- (a) a copolymerisation step, in which a monomer mixture, comprising MMA, a monomer of formula (I), and, optionally, at least one optional co-monomer c), undergoes radical copolymerisation to form the copolymer, wherein the reaction temperature in
 30 copolymerisation step (a) is above 100 °C, preferably above 120 °C and wherein the monomer mixture comprises at least 10 mol-%, preferably at least 20 mol-%, based on the total monomer mixture, of at least one monomer represented by formula (I)



wherein the substituents R^1 , R^2 , R^{2a} , R^3 and R^{3a} are independently represented by a hydrogen atom, a hydrocarbon group having from 1 to 12 carbon atoms; a hydroxy group; a hydroxy alkyl group; a carboxylic group; $-C(=O)-NH_2$; $-C(=O)-R^x$; $-C(=O)-O-R^x$; with R^x is C1-12-alkyl or C6-12-cycloalkyl; or R^2 and R^3 can build together a cyclic moiety.

11. Process according to Claim 10, wherein the reaction temperature in copolymerisation step (a) is in the range from 100 °C to 200 °C, preferably from 120 °C to 180 °C.
12. Process according to Claim 10 or 11, wherein the monomer mixture comprises from 10 to 70 mol-%, preferably from 20.0 to 60.0 mol-%, based on the total amount of polymerizable components, of at least one monomer represented by formula (I).
13. Process according to any of Claims 10 to 12, wherein the monomer mixture in the copolymerisation step (a) has the following composition, based on the total amount of polymerizable components:
 - a) from 30.0 to 90.0 mol-%, preferably 40.0 to 80.0 mol-%, of methyl methacrylate;
 - b) from 10.0 to 70.0 mol-%, preferably 20.0 to 60 mol-%, of the compound represented by formula (I); and
 - c) from 0.0 to 15.0 mol-%, preferably 0.0 to 10 mol-%, of at least one optional co-monomer c) selected from acrylic acid, methacrylic acid, vinyl aromatic monomers, alkyl acrylates and alkyl methacrylates different from methyl methacrylate.
14. Process according to any of Claims 10 to 13, wherein the copolymerisation step (a) is carried out as bulk polymerisation.
15. Process according to any of Claims 10 to 14, wherein the copolymerisation step (a) is followed by
 - (b) a step of heating the copolymer solution obtained in the polymerisation step (a) to a temperature from 100 °C to 300 °C and
 - (c) a step of removal of volatile components in a degassing apparatus.
16. Moulding composition comprising a copolymer according to any of Claims 1 to 9 and at least one additive selected from UV absorbers, UV stabilizers, antioxidants, colourants, flow improver, scattering aids, lubricants, demoulding aids or a combination of any of those.
17. Moulded article produced from the moulding composition according to claim 16, wherein the moulded article is selected from display components; lighting components; components in the automotive exterior; components in the automotive interior; components for optoelectronic

devices; components for optical sensors; components for solar cells; optical elements; and components for medical devices having a light source.