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Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report (Art. 21(3))*

WO 2020/254460 A1

(54) **Title:** METHOD FOR PRODUCING GLYCEROL MONO(METH)ACRYLATE

(57) **Abstract:** The invention relates to a method for producing glycerol mono(meth) acrylate from 2,2-dimethyl-1,3-dioxolan-4-yl-methyl (meth)acrylate by acidic silica catalysed reaction with methanol.

Method for producing glycerol mono(meth)acrylate

Field of the invention

The invention relates to an anhydrous method for producing glycerol mono(meth)acrylate by reacting 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate with methanol.

Prior art

Glycerol mono(meth)acrylate can be used for various industrial applications, for example as a monomer for producing polymers for coating purposes, varnishes, paints, adhesives or contact lenses, as well as in the field of oil-based lubricants and slip additives.

For many applications it is critical that glycerol mono(meth)acrylate is in the form of high-purity monomer since even trace impurities can firstly result in negative effects during storage of the monomer and these secondly also impair the quality of the polymer to be produced.

Particularly undesirable impurities in monomers are those which may act as crosslinkers in a polymerization reaction since the presence of crosslinkers during a polymerization reaction impairs the formation of linear polymers. Even traces of acids considerably reduce the stability of the monomer.

Glycerol mono(meth)acrylate can, in principle, be obtained by various routes.

Firstly, glycerol can be esterified directly with acetylating reagents (e.g. methacrylic acid, methacrylic anhydride, methacryloyl halides). For example, WO 2018/031373 describes the preparation of glycerol monomethacrylate (GMMA) from glycerol and an excess of methacrylic acid in the presence of amberlyst. However, in this case, low selectivity is problematic.

More selective with respect to monofunctionalization is the mostly acid-catalysed epoxide and acetonide cleavage of glycidyl methacrylate or 2,2-dimethyl-1,3-dioxolan-4-ylmethyl methacrylate (IPGMA) in aqueous medium to give GMMA, wherein the cleavage of the harmful to health glydicyl methacrylate leads to the formation of undesired by-products (*J. Appl. Polym. Sci.*, 135, 46579) or requires a laborious column chromatographic purification (Macromolecules 2018, 51, 18, 7396-7406).

The preparation of GMMA by hydrolysis of IPGMA is described, for example, in GB 852 384, wherein the hydrolysis is carried out in the presence of dilute aqueous solutions of strong mineral acids.

In US 2010/249352, the acetonide is cleaved in aqueous medium by addition of an acid, and is then neutralized with a weak base. The water is removed in a laborious process of multiple distillation on a thin-film evaporator.

The preparation of GMMA from IPGMA is also described in DE102016122755. The preparation is also carried out here in aqueous medium in the presence of amberlyst and with simultaneous feed of an O_2/N_2 gas stream.

GMMA can also be obtained via lipase-catalysed transacylation (*J. Mol. Cat. B: Enzymatic* **2010**, *62*, 80-89), which requires utilization of enzymes and long reaction times (120 h) and has low conversions.

The methods described above have the addition of water in common, which is very difficult to remove from the remaining reaction mixture/product. The consequence is a high residual water content in the product, which has a negative effect on the further use of glycerol mono(meth)methacrylate or can even completely prevent it. In addition, polymerization occurs during the dewatering phase owing to the prolonged thermal stress.

Particularly for the application of glycerol mono(meth)acrylate in the field of oil-based lubricants and slip additives, water can also be included among the particularly undesirable impurities. In the field of lubricants and hydraulic oils - in addition to contamination with solid particles - contamination with water or moisture can be the cause of component failure.

Water may mix with oil in different ways. At low concentrations, it can be dissolved in oil in the liquid phase and thus may not be visually noticeable (solubility in the range of several hundred ppm, material-dependent and age-dependent): It takes the form of a one-phase system. On further increasing the water content, the solubility limit is exceeded and (microscopically) small droplets are formed in the oil, which is known as an emulsion. The water content has in this case exceeded the saturation point, which results in a distinct and undesirable cloudiness of the oil. On further increasing the water content, this eventually results in the formation of two phases, namely a low-oil water phase and a low-water oil phase.

In the sector of lubricants and hydraulic oils, particularly free water and emulsified water have an adverse effect on the material characteristics, for example on the compressibility. Even low levels of impurities in the range of 1% can result in drastic shortening of the service life of the oil. In moving bearings, the formation of a stable oil film is prevented by water contamination. Furthermore, under high temperature and pressure load, there can be spontaneous evaporation of the water (and thus oil), which results in erosive wear. Oil contamination by water further causes foam formation, oil hydrolysis, metal embrittlement, rust and corrosion.

For the use of glycerol mono(meth)acrylate in oil-based systems, the aim is therefore the lowest possible water content in glycerol mono(meth)acrylate, which cannot be achieved for this hydrophilic monomer by means of current synthetic methods.

The object of the invention, therefore, was to provide an improved method for producing glycerol mono(meth)acrylate, by means of which the problems described above with respect to selectivity and by-product formation can be overcome, in which no toxic starting materials have to be used and in which no laborious dewatering step is required. Ideally, the glycerol mono(meth)acrylate product also should not comprise any traces of acid.

By means of this method, a crosslinker-free and the purest possible glycerol mono(meth)acrylate should be obtained without the use of mutagenic substances.

Moreover, the method should be achievable on an industrial scale.

Summary of the invention

The object is achieved in that glycerol mono(meth)acrylate is produced by a silicate catalysed cleavage of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate with methanol.

Accordingly, the method relates to a method for producing glycerol mono(meth)acrylate, particularly glycerol monomethacrylate (GMMA), characterized in that 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate, especially 2,2-dimethyl-1,3-dioxolan-4-ylmethyl methacrylate (IPGMA), is reacted with methanol in the presence of an acidic silicate catalyst.

In this manner, anhydrous glycerol mono(meth)acrylate is obtained without using glycidyl methacrylate that is harmful to health. By avoiding an initial water input to the reaction mixture, a time- and energy-intensive removal of water from the end product is avoided. Also, a prolonged dewatering phase and thus accompanying polymerization of the monomer is prevented.

Detailed description of the invention

The invention relates to both glycerol monomethacrylate (GMMA) and glycerol monoacrylate (GMA). Accordingly, the term glycerol mono(meth)acrylate, as used in the context of this invention, includes both GMMA and GMA.

The ratio by weight of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate to methanol in the method according to the invention should be in the range from 1:1 to 1:20, preferably from 1:1 to 1:15 and particularly preferably in the range from 1:1 to 1:4.

For the reaction, both technical-grade methanol and high purity methanol with a purity of 99.9% can be used.

Particularly suitable silicate catalysts include clay minerals such as montmorillonite, kaolinite, hectorite, halloysite or mixtures thereof, for example bentonite. Particular preference is given to using acidic sheet silicates and aluminium silicates, such as Tonsil® 312 FF or montmorillonite K10, K30 etc. The catalysts used are particularly particles with the greatest possible specific surface area, particularly with specific surface areas greater than 50 m^2/g, preferably with a specific surface area greater than 220 m^2/g, and particularly preferably with a specific surface area greater than 320 m^2/g.

Compared to homogeneous-catalysed acetonide cleavage of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate with p-TsOH (para-toluenesulfonic acid) or the heterogeneous-catalysed acetonide cleavage of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl (meth)acrylate with acidic ion exchange resins (Amberlyst®), an exceptionally low-crosslinker glycerol mono(meth)acrylate product is obtained particularly when using silicate-based catalysts: contamination with glycerol di(meth)acrylate is less than 1%. The product is also virtually free of free glycerol (< 1%), which is also found in greater amounts in conventional synthetic routes.

Preferably, the reaction is performed in anhydrous manner and the product is anhydrous glycerol mono(meth)acrylate.

The acidic silicate catalyst is used in an amount of 0.5% by weight to 20% by weight, preferably in an amount of 1% by weight to 15% by weight, and especially in an amount of approximately 10% by weight, based on the reaction batch.

Pre-treatment of the catalyst is generally not required.

For stabilizing the starting material and/or product, stabilizers/polymerization inhibitors may be used.

Preferred polymerization inhibitors that can be used include, inter alia, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, phenothiazine, hydroquinone, hydroquinone monomethyl ether, 4-hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL), 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, para-substituted phenylenediamines such as for example N,N'-diphenyl-p-phenylenediamine, 1,4-benzoquinone, 2,6-di-tert-butyl-alpha-(dimethylamino)-p-cresol and 2,5-di-tert-butylhydroquinone. These compounds can be used individually or in the form of mixtures and are generally commercially available. The mode of action of the stabilizers is usually that they act as free-radical scavengers for the free radicals that occur in the polymerization. Further details can be found in the relevant technical literature, particularly Römpp-Lexikon Chemie; publisher: J. Falbe, M. Regitz; Stuttgart, New York; 10th edition (1996);

keyword “Antioxidantien” and the literature references cited therein.

The total amount of stabilizers used is between 0.0001% by weight and 0.5% by weight, preferably in the weight range between 0.001% by weight and 0.05% by weight.

Preferably, the stabilizers hydroquinone monomethyl ether and hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL) are used in combination. The ratio of hydroquinone monomethyl ether to TEMPOL is ideally in the range between 15:1 and 1:1, preferably in the range between 10:1 and 4:1.

In addition, gaseous oxygen can be used for stabilization. This can, for example, be in the form of air, in which the amounts introduced should be adjusted such that the content in the gas phase above the reaction mixture remains below the explosion limit.

The reaction times depend, inter alia, on the selected parameters such as pressure and temperature. In general, however, they are in the range from 1 to 65 hours, preferably 5 to 24 hours and especially preferably 5 to 22 hours. In the continuous processes, the residence times are generally in the range of 5 to 24 hours, preferably 5 to 22 hours.

The reaction can be carried out preferably while stirring, wherein the stirring speed is in the range of 50 to 2000 rpm and preferably in the range of 100 to 500 rpm.

The reaction is ideally carried out at standard pressure. The reaction temperature is between 20°C and 80°C, preferably between 40°C and 70°C.

The method according to the invention can be operated industrially, specifically both in continuous/semi-continuous mode and batchwise mode.

In comparison to the methods known from the literature, glycerol mono(meth)acrylate is obtained by the method according to the invention not only in anhydrous, but also in highly pure form.

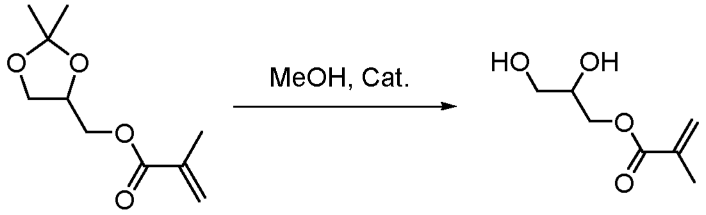
The glycerol mono(meth)acrylate obtained by the method according to the invention can be used in applications which require a low residual water content or even the complete absence of water. In particular, it can be used in oil-based systems in the sector of lubricants and hydraulic oils, and in polymerization reactions in liquid and hydrophobic media.

The following examples illustrate the method according to the invention without these being limited thereto.

Examples

Apparatus: 500 ml stirring apparatus, air inlet, Büchi rotary evaporator with vacuum accessories, pressure filter. Magnetic stirrer, oil pump.

Reaction:



Mixture:	50	g	of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl methacrylate (IPGMA)	=	0.25 mol
	80	g	of methanol	=	2.5 mol
	0.016	g	of hydroquinone monomethyl ether rel. to GMMA	=	400 ppm
	0.004	g	of hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL); rel. to GMMA	=	100 ppm
	13	g	of catalyst/Tonsil® 312 FF standard rel. to mixture	=	10%

Procedure:

The batch is boiled at 65°C under reflux with stirring for 20 h. The GMMA crude ester obtained is filtered through a pressure filter with K800 filter layer. The filter is rinsed with ca. 100 g of methanol. The clear, pale yellow GMMA crude ester is freed of solvent at 50°C bath temperature at 20 mbar on a rotary evaporator for 30 min.

Results:

					Reaction			GMMA GC-RV in area%						
	IPGMA mol	MeOH mol	Catalyst	% by weight rel. to mixture	Duration h	Bottoms max. °C	Mass g = % of theory	MeOH	IPG	IPGMA	Glycerol	Glycerol dimethacrylate	GMMA	Remarks
1	0.25	2.5	**Amberlyst® A15 washed and dried** **LJ: 20896/57**	10	20	50	43g = 38%	-	9.3	0.4	16.4	16.5	**35.9**	**Clear dark product**
2	0.25	2.5	**p-TS**	1	22	50	43g = 8%	-	26.5	2.9	25.2	8.9	**7.8**	**Clear yellow product --> polymer**
3	0.25	2.5	**Montmorillonite K10**	10	22	50	41g = 58%	3.0	1.0	34.2	0.8	0.1	**56.6**	**Clear yellow product**
4	0.25	2.5	**Montmorillonite K10**	10	5	50	41g = 59%	2.3	0.6	37.4	0.5	< 0.1	**58.0**	**Clear yellow product**

5	0.25	2.5	**Montmorillonite K30**	10	5	65	42g = 69%	0.1	1.1	26.1	1.6	0.1	**65.3**	**Clear yellow product**
6	0.25	2.5	**Tonsil® 312 FF**	10	22	50	41g = 68%	0.6	0.5	31.2	0.4	-	**66.6**	**Clear pale yellow product**
7	0.25	2.5	**Tonsil® 312 FF**	10	64	RT	44g = 65%	2.2	0.5	38.0	0.4	-	**58.7**	**Clear pale yellow product**
8	0.25	2.5	**Tonsil® 312 FF**	10	20	65	43g = 79%	2.3	0.5	22.3	0.6	< 0.1	**73.1**	**Clear pale yellow product**

Claims

1. A method for producing glycerol mono(meth)acrylate, **characterized in that** 2,2-dimethyl-1,3-dioxolan-4-yl methyl (meth)acrylate is reacted with methanol in the presence of an acidic silicate catalyst.

2. Method according to Claim 1, **characterized in that** the silicate is a sheet silicate or a mixture of sheet silicates.

3. Method according to Claim 2, **characterized in that** the sheet silicate or the mixture of sheet silicates have a specific surface area greater than 50 m^2/g, preferably greater than 220 m^2/g and particularly preferably greater than 320 m^2/g.

4. Method according to Claim 2 or according to Claim 3, **characterized in that** the sheet silicate or the mixture of sheet silicates is selected from the group consisting of montmorillonite, kaolinite, hectorite, halloysite and bentonite.

5. Method according to any of Claims 2 to 4, **characterized in that** the sheet silicate or the mixture of sheet silicates is montmorillonite or bentonite.

6. Method according to any one of the preceding claims, **characterized in that** the reaction is performed in anhydrous manner and in that the product is anhydrous glycerol mono(meth)acrylate.

7. Method according to any of the preceding claims, **characterized in that** the acidic catalyst is used in an amount from 1% by weight to 15% by weight, based on the reaction batch.

8. Method according to any of the preceding claims, **characterized in that** at least one stabilizer is used selected from the group consisting of octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, phenothiazine, hydroquinone, hydroquinone monomethyl ether, 4-hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL), 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, para-substituted phenylenediamines such as for example N,N'-diphenyl-p-phenylenediamine, 1,4-benzoquinone, 2,6-di-tert-butyl-alpha-(dimethylamino)-p-cresol, 2,5-di-tert-butylhydroquinone.

9. Method according to Claim 8, **characterized in that** the total amount of stabilizers used is between 0.001% by weight and 0.5% by weight.

10. Method according to either of Claims 8 and 9, **characterized in that** the stabilizers hydroquinone monomethyl ether and hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL) are used in combination.

11. Method according to Claim 10, **characterized in that** the ratio of hydroquinone monomethyl ether to TEMPOL is in the range between 10:1 and 4:1.

12. Method according to any of the preceding claims, **characterized in that** the reaction temperature is between 20°C and 80°C.

13. Method according to Claim 12, **characterized in that** the reaction temperature is between 40°C and 70°C.

14. Glycerol mono(meth)acrylate having a content of glycerol di(meth)acrylate of less than 1 % and a content of glycerol of less than 1 %.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/066865

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/29
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUERVY C. O. SOUSA ET AL: "Microwave-promoted morita-baylis-hillman reactions: efficient synthesis of new monoacylglycerols (MAGs) as potential anti-parasitic compounds", JOURNAL OF THE BRAZILIAN CHEMICAL SOCIETY, vol. 22, 1 January 2011 (2011-01-01), pages 1634-1643, XP055630834, São Paulo; BR ISSN: 0103-5053, DOI: 10.1590/S0103-50532011000900003	1-13
Y	page 1637 -----	1-13
Y	DE 103 08 504 A1 (BASF AG [DE]) 9 September 2004 (2004-09-09) paragraphs [0072] - [0077] -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 16 July 2020	Date of mailing of the international search report 22/09/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Grassi, Damian

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2020/066865

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-13

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

Process according to claims 1-13.

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2. claim: 14

Glycerol mono(meth)acrylate according to claim 14.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/066865

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 10308504 A1	09-09-2004	AT 363540 T	15-06-2007
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		WO 2004076676 A1	10-09-2004