

Process for preparing N-methyl(meth)acrylamide

5 The invention relates to a process for preparing N-methyl(meth)acrylamide.

N-Methyl(meth)acrylamide can be prepared by reaction with acid halide and methylamine. In this case, however, an additional equivalent of base is required, by which the hydrogen halide formed is scavenged. In the case of doubt, this is methylamine itself, which would require two equivalents of
10 methylamine, which would adversely affect the economic viability of the preparation.

A further preparation is described in general terms by DE4027843, a continuous process for preparing N-substituted acrylamides and methacrylamides. In this process, by reaction of alkyl esters of acrylic acid or methacrylic acid with aliphatic or aromatic amines in a molar ratio of 1:≥ 2
15 in continuous mode, the corresponding N-substituted acrylamides and methacrylamides are obtained. Like the preparation with acid chlorides, this process requires two equivalents of the amine and is therefore only of limited atom economy. Although the reaction does not need a catalyst, it proceeds under severe conditions at > 150°C and a pressure of about 160 bar. If N-methylmethacrylamide is prepared with more amine than the stoichiometric amount of methacrylic
20 anhydride, a vacuum-unstable salt is formed. In the subsequent workup, it breaks down, and so the vacuum cannot be maintained, the temperature rises in an uncontrolled manner and the product ultimately polymerizes.

DE102011089363 likewise discloses the preparation of N-alkyl(alkyl)acrylamides, likewise
25 proceeding from the corresponding acid anhydride and alkylamine. What is claimed here is the addition of the amine in aqueous solution, and neutralization of the solution prior to removal of the product. For the preparation of N-methyl(meth)acrylamide, preparation in aqueous solution is very unfavourable. N-Methyl(meth)acrylamide is a liquid, dissolves in water in any ratios, can only be extracted with great difficulty and results in very high losses owing to similar boiling points on
30 distillative separation. However, the use of aqueous solutions of the amine has the crucial advantage that the ammonium salt of the acid formed as an intermediate is forced into a dissociation equilibrium in the presence of water. As a result, there are always small traces of amine in the system, which can react with the anhydride, such that the overall yield reaches > 95%.

35 WO 2010/021956 discloses the preparation of N-alkyl(alkyl)acrylamides, likewise proceeding from the corresponding acid anhydride and alkylamine. What is claimed here is the addition of the anhydride to the amine in the form of an initially charged aqueous solution. This process variant is

associated with significant exothermicity, which can cause discolouration. Furthermore, the same disadvantages exist as in DE102011089363.

The problem addressed was that of providing a particularly economically reliable process for preparing N-methyl(meth)acrylamide.

The problem was solved by a process for preparing N-methyl(meth)acrylamide by reacting (meth)acrylic anhydride and methylamine in the absence of water.

More particularly, the problem was solved by a process for preparing N-methyl(meth)acrylamide, characterized in that

- a) (meth)acrylic anhydride is reacted with methylamine,
- b) the methylamine has a water content of < 10% by weight,
- c) the stoichiometry of anhydride:amine is less than 1:2.

It has been found that, surprisingly, the process according to the invention achieves virtually quantitative yields, and the losses on workup to give a pure material are particularly low. Moreover, the (meth)acrylic acid by-product can be reused as starting material for the preparation of the anhydride, and so the reaction has complete atom economy and is thus not just particularly efficient but also very sustainable.

It has been found that the process according to the invention can be conducted particularly advantageously when the reaction is virtually anhydrous.

Furthermore, it has been found that the reaction can be conducted without addition of catalyst, which leads to a further improvement in the economic viability of the process.

The notation "(meth)acrylate" here means both methacrylate, for example methyl methacrylate, ethyl methacrylate, etc., and acrylate, for example methyl acrylate, ethyl acrylate, etc., and mixtures of the two.

Catalyst

The reaction can be conducted in the absence of catalysts. The reaction is sufficiently rapid without addition of catalyst.

(Meth)acrylic anhydride

(Meth)acrylic anhydride used is methacrylic anhydride or acrylic anhydride.

Stabilizer

The (meth)acrylic anhydride is preferably used in stabilized form. Suitable stabilizers are: phenothiazine, 2,4-dimethyl-6-tert-butylphenol, N,N'-diphenyl-p-phenylenediamine, 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl, 4-methyl-2,6-di-tert-butylphenol, 2-tert-butyl-6-(3-tert-butyl-2-
5 hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, benzene-1,4-diamine, N,N'- mixed phenyl and tolyl derivatives (DTPD), 2,6-di-tert-butyl- α -(dimethylamino)-p-cresol, tert-butylcatechol, bis-2,2,6,6-tetramethyl-4-piperidyl sebacate, 2,2,6,6-tetramethylpiperidine N-oxyl and mixtures thereof.

10 The amount of stabilizer is introduced into the reactor with (meth)acrylic anhydride as a solution at the start of the reaction, initially charged or added after the (meth)acrylic anhydride.

Methylamine

15 Methylamine can be used in liquid form, in gaseous form (for example monomethylamine, from GHC Gerling, Holz + Co, Hanau, Germany) or in anhydrous solvents, for example in THF, MTBE, acetonitrile, chloroform, dichloromethane or diethyl ether. Aqueous methylamine solutions are unsuitable for this process.

20 Preferably, the water content of the methylamine is < 10% by weight, preferably < 5% by weight, more preferably < 1% by weight and most preferably < 0.1% by weight.

25 Preferably, the water content of the reaction mixture after the end of addition of all reactants is < 10% by weight, preferably < 5% by weight, more preferably < 1% by weight and most preferably < 0.1% by weight.

Solvent

30 The reaction can be effected without solvent, or in the presence of solvents. Suitable solvents are selected from the group of: THF, MTBE, diethyl ether, dioxane, acetonitrile, nitromethane, chloroform, dichloromethane, benzene or toluene and mixtures thereof.

Reaction conditions

35 The reaction is effected at temperatures between -20°C and 100°C, preferably between 0°C and 80°C and more preferably between 20°C and 50°C.

To avoid the formation of unwanted by-products, a particularly low temperature is employed in order to prevent the Michael addition of amines onto the double bond of the (meth)acrylate.

The (meth)acrylic anhydride is reacted with methylamine at an absolute pressure of 0.5 bar to 10 bar, preferably 1 bar to 5 bar.

The reaction time is in the range of 0.1-10 h, preferably 0.5-5 h.

5

Stoichiometry

The stoichiometry of (meth)acrylic anhydride:amine is less than 1:2, preferably less than 1:1.5, more preferably less than 1:1.1 and most preferably exactly 1:1.

10

In a further process version in which ambient pressure is employed, it is also possible to bubble methylamine into the reaction solution. In this case, not all the methylamine reacts. What is crucial to the success of the reaction is that the excess of the amine reacted to (meth)acrylic anhydride is between 0.5 and 1.5.

15

Neutralization and workup:

The crude product obtained can be worked up directly after the end of the reaction by means of a fractional distillation without any need for neutralization.

20

Preferred method variants

The (meth)acrylic anhydride is initially charged in an autoclave and the autoclave is screwed shut. The steel methylamine gas bottle is connected to the autoclave by a coiled VA feed pipe, and the decrease in weight on introduction of methylamine is monitored.

25

The introduction of methylamine is commenced with a feed rate of about 4 g/3 min at room temperature. The reaction is strongly exothermic. The temperature should not exceed 40°C (35°C ± 5°C). The mixture is cooled with an acetone-dry ice mixture. The metering rate is increased to 6 g/3 min of methylamine. Once the stoichiometric amount of methylamine has been introduced, the bottle is closed, the remaining gas in the conduit is left to react for 10 min and then the cooling is removed and the autoclave is vented.

30

An alternative method is reaction in the presence of solvents. (Meth)acrylic anhydride and a suitable solvent, for example MTBE, are initially charged and cooled. The methylamine gas is introduced at about 2°C-10°C. The reaction is weakly exothermic.

35

Since the reaction proceeds only very gradually at this temperature, gas may be introduced at a faster rate. The bottom temperature can rise to up to 50°C. The introduction is ended when no

(meth)acrylic anhydride is detectable any longer. The solvent is drawn off, for example with a rotary evaporator. The residue is distilled.

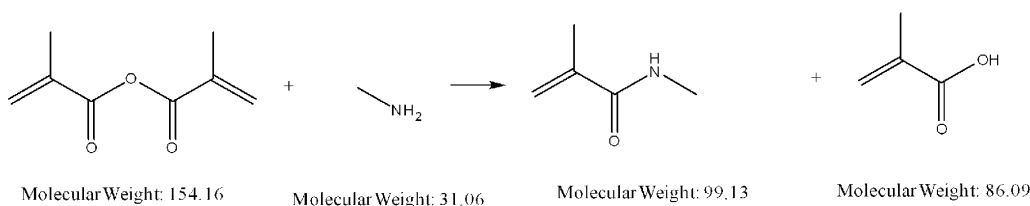
The N-methyl(meth)acrylamides prepared in accordance with the invention find use as copolymer in (meth)acrylate polymers in order to increase the water solubility of a polymer.

The examples given hereinafter are given for better illustration of the present invention, but are not capable of restricting the invention to the features disclosed therein.

The methacrylic anhydride used in the present examples has always been stabilized with 2000 ppm of 2,4-dimethyl-6-tert-butylphenol.

Example 1: Preparation of N-methylmethacrylamide

Reaction equation:



Apparatus: 2 L autoclave with glass insert, Ni-Cr-Ni thermocouple, gas feed: metal, steel methylamine gas bottle, manometer, acetone/dry ice bath

Mixture:

6.0	mol	methacrylic anhydride	=	940.2	g
6.0	mol	methylamine, gas	=	186.4	g

Theoretical yield: (= starting weight) 1126.6 g

Procedure: The methacrylic anhydride is initially charged in the glass insert of the autoclave and the autoclave is screwed shut. The steel methylamine gas bottle is on a balance and is connected to the autoclave by a coiled VA feed pipe; hence the decrease in weight on introduction of methylamine can be monitored.

The introduction of methylamine is commenced with a metering rate of about 4 g/3 min at room temperature. The reaction is strongly exothermic. The temperature should not exceed 40°C (35°C ± 5°C). The mixture is cooled with an acetone-dry ice mixture. The metering rate is increased to 6 g/3 min of methylamine; no more is possible due to the cooling as a result of the poor heat

transfer owing to the glass insert. Once the stoichiometric amount of methylamine (186.4 g, 6 mol) has been introduced, the bottle is closed, the remaining gas in the conduit is left to react for 10 min and then the cooling is removed and the autoclave is vented.

5 Yield: 1125 g

GC of the product, method: (GC: DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min ->280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

Name	Methyl-amine	Methacrylic acid	N-Methyl-methacrylamide	Methacrylic anhydride	HB
Retention:	1.08 min	3.83 min	5.97 min	7.43 min	13.15 min
GC area%	0.045	41.360	52.445	0.079	4.187

HB = high boilers

10

Example 2: Workup of N-methylmethacrylamide by distillation

15 **Apparatus:** 2 l three-neck round-bottom flask with boiling capillary, Pt100 temperature sensor, 30 cm mirrored column with 8 x 8 Raschig rings, automatic column head (liquid divider), reflux condenser, coiled condenser, Thiele-Anschütz attachment, receivers, oil bath, vacuum pump, manometer

Mixture:

20 1122 g N-methylmethacrylamide from Example 1
 22.4 mg 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (rad.) (20 ppm)
 224.4 mg hydroquinone monomethyl ether (200 ppm)
 1122 mg octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (1000 ppm)

Procedure:

Bath °C	Bottom °C	Top °C	Pressure mbar	Comment
28	28	28	13.0	start of heating
108	88.9	50	4.0	boils, RR 1:5; 1st fraction
111	99.2	58	3.8	2nd fraction
112	100.4	62	3.8	3rd fraction
128	114.7	69	2.9	4th fraction
134	119.6	89	2.8	5th fraction
136	113	91	2.9	RR 1:10
141	118	91	2.8	RR 1:5
146	122	94	2.8	6th fraction
147	122.6	94	2.7	7th fraction
131	104	77	2.4	8th fraction
138	105.9	79	2.3	9th fraction
139	106.4	79	2.3	10th fraction
144	108.5	79	2.3	RR 1:2.5
144	108.0	80	2.3	RR 1:1
143	110.4	81	2.3	11th fraction
153	130	77	2.3	end

RR = reflux ratio

Yield and GC analyses:

Name	Amount g	Methyl-amine	Methacrylic acid	N-Methyl-methacryl-amide	Methacrylic anhydride	HB 2	HB 3	HB 1
Retention: [min]		1.08 min	3.83 min	5.97 min	7.43 min	8.71	10.89	13.15
Fraction								
1st	135.7	0.003	99.867	0.124				
2nd	139.1	0.007	99.993					
3rd	84.2	0.004	99.938	0.037				
4th	50.4		97.275	1.758	0.008	0.77		
5th	58.0	0.018	62.601	33.538	0.007	3.44		
6th	28.8		38.609	56.422	0.008	4.52		
7th	30.4		22.935	72.339	0.005	4.30		
8th	73.3		7.300	90.296		2.12		
9th	38.5		3.850	94.531		1.15	0.011	
10th	230.3		0.929	98.566		0.36	0.060	0.011
11th	113.6		0.116	99.120		0.23	0.339	0.053
Cold trap 1	8.5	0.004	99.921	0.067				
Cold trap 2	1.5	0.027	65.237	30.016		3.97		
Residue *	75.6		1.285	14.950			3.100	20.60

* viscous, further peaks: 11.257 min: 25.653%; 11.688 min: 15.458%; 12.259 min: 5.177% + further smaller peaks

Example 3: Preparation of N-methylmethacrylamide in solvent

- Apparatus:** 1 l four-neck round-bottom flask with precision glass stirrer (Teflon sleeve), Pt100
 5 temperature sensor, gas inlet (Teflon), gas outlet of Teflon with wash bottles as safety bottles, reflux condenser, steel methylamine gas bottle, waste air conduit directly into the fume hood, feed for compressed air as added air, acetone/dry ice cooling bath

Mixture:

- 10 1.0 mol methacrylic anhydride = 156.4 g
 250 ml methyl tert-butyl ether (MTBE)
 1.0 mol methylamine, gas

Theoretical yield: 99.1 g

- 15 **Procedure:** Methacrylic anhydride and MTBE are initially charged and cooled. The methylamine gas is introduced at about 2°C-10°C. The reaction is weakly exothermic.
 Since the reaction proceeds only very slowly at this temperature, gas is introduced more quickly and the bottom temperature can be increased to up to 50°C. The introduction is ended when no methacrylic anhydride is detectable any longer. The MTBE is drawn off on a rotary evaporator (RE)
 20 at a bath temperature of 60°C and a pressure down to 200 mbar.
 Distillate to 200 mbar: 151.5 g
 Residue to 200 mbar: 181.7 g

- The residue (180 g) is distilled through a 15 cm Vigreux column under reduced pressure with
 25 addition of 1000 ppm of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 500 ppm of hydroquinone monomethyl ether and 20 ppm of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (rad.).

Bath [°C]	Bottom [°C]	Top [°C]	Pressure mbar	Comment	Mass
24	24	24	3.8	start of heating	
83	64.7	53	2.1	1st fraction	62.9 g
85	70.5	64	1.8	2nd fraction	35.3 g
90	72.3	69.0	1.7	3rd fraction	45.0 g
92	75.2	71	1.6	4th fraction	19.7 g
103	84.3	70	1.6	Thermometer no longer immersed	
111	96.9	50	1.6	end	13.5g

Analyses: (GC: DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min ->280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

Name	MTBE	Methyl-amine	Methacrylic acid	N-Methylmeth-acrylamide	Methacrylic anhydride	HB 1
Ret. [min]	1.33	1.08	3.83	5.97 min	7.43 min	13.15
Probe:						
Rct: 1.5 h	*		3.38	2.96	89.70	2.18
Rct: 3 h	*		14.82	16.23	59.33	4.19
Rct: 5 h	*		37.09	45.68	9.53	3.59
Rct: 5.5 h	*		40.80	51.43	0.05	3.05
RE distillate	98.63		1.27	0.11		
RE residue		0.06	39.95	53.65	0.01	3.87
Dist. 1st fr.	0.02	0.02	85.52	14.26	0.01	0.02
Dist. 2nd fr.		0.04	37.91	61.80		0.10
Dist. 3rd fr.	0.03	0.05	10.45	88.92		0.29
Dist. 4th fr.		0.05	1.67	96.71		0.93

* not included in integration

5

Yield via GC analyses: 89.9 g of N-methylmethacrylamide = 90.7% of theory

Comparative Example 1: Preparation of N-methylmethacrylamide in excess methylamine gas

Apparatus: 1 l four-neck round-bottom flask with precision glass stirrer (Teflon sleeve), Pt100 temperature sensor, gas feed of Teflon with wash bottles as safety bottles, gas inlet (Teflon), reflux condenser, steel methylamine gas bottle, waste air conduit directly into the fume hood, feed for compressed air as added air, acetone/dry ice cooling bath

Mixture:

1.0 mol methacrylic anhydride = 156.4 g

250 ml methyl tert-butyl ether

~2 mol methylamine, gas

Theoretical N-methylmethacrylamide yield: 99.1 g

Procedure: Methacrylic anhydride and MTBE are initially charged, and methylamine gas is introduced with vigorous stirring. The conversion is monitored by GC. If no methacrylic anhydride is detectable any longer, methylamine is nevertheless introduced further, since an exothermic reaction is still taking place. As soon as this becomes weaker, the introduction is ended. After the stirring has been stopped, 2 phases form. The MTBE is drawn off on a rotary evaporator at bath temperature 60°C and a pressure down to 200 mbar.

Distillate to 200 mbar: 177.1 g

Residue to 200 mbar: 215.0 g

	MTBE 1.328 min	Methyl- amine 1.08 min	Methacrylic acid 3.83 min	N- Methylmeth -acrylamide 5.97 min	Methacrylic anhydride 7.43 min
1h 5 min	*		10.35	11.15	73.14
2h 15 min	*		20.19	23.34	49.91
3h 15 min	*		27.59	32.88	32.24
4h 15 min	*	1.70	40.17	51.52	-
5h 15 min	*	5.98	37.83	46.93	-
Lower phase	*	8.67	35.92	45.36	
Upper phase	*	10.55	11.36	68.47	
Distillate to 200 mbar	98.01	1.99			
Residue to 200 mbar		7.36	36.33	46.47	
Distillation of 1st fraction		2.42	34.07	63.32	

* not included

5

180 g of the rotary evaporator residue is distilled through a 15 cm Vigreux column under reduced pressure with addition of 1000 ppm of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 500 ppm of hydroquinone monomethyl ether and 20 ppm of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (rad.).

- 10 Owing to the breakdown of methylammonium methacrylate, the pressure can no longer be maintained from a bottom temperature of 40°C. From a bottom temperature of 90°C, mist forms in the receiver and the apparatus. This is a clear sign of the reaction of an amine with acid. Immediately after a distillate has been obtained, a solid forms in the bottom and the mixture polymerizes completely within 10 min.

15

Time	Bath °C	Bottom °C	Top °C	Pressure mbar	Comment
10:24	25	25	25	1.6	start of heating
10:37	81	60.5	27	7.4	
10:58	117	92.2	45	13.1	
10:59	121	94.7	59	13.0	mist in receiver
11:01	121	97.5	80	13	1st fraction, lumps in the liquid phase
11:03	123	95.6	71	4.1	
11:10	129	89.7	68	2.5	stopped, bottoms polymeric

Yield: Fraction 1: 16.2 g

- 20 **Comparative Example 2: Preparation of N-methylmethacrylamide from aqueous methylamine**

Apparatus: 2 l four-neck round-bottom flask with precision glass sabre stirrer, 500 ml dropping funnel, Pt-100 liquid phase thermometer, reflux condenser, cooling bath

Mixture:

- | | | | |
|---|----------|--------------------------------------|-----------|
| 5 | 6.15 mol | methacrylic anhydride | = 961.5 g |
| | 6.15 mol | methylamine, 40% in H ₂ O | = 477.4 g |

Theoretical yield: 609.65 g

Procedure:

- 10 Methacrylic anhydride is initially charged and cooled to below 10°C while stirring. Then the metered addition of methylamine is commenced (exothermic reaction, ice bath cooling and slight mist formation). Dropwise addition and cooling are effected such that the temperature does not rise above 10°C. After dropwise addition has ended (4 h), stirring is continued for another 2 h for further reaction; the cooling is removed.

Workup:

The mixture (1419 g) is concentrated on a rotary evaporator with addition of 1000 ppm of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 500 ppm of hydroquinone monomethyl ether and 20 ppm of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (rad.).

- 20

Residue in the flask:	229.7 g
Distillate to 35 mbar, bath 80°C	340.8 g
Distillate to 5 mbar, bath 80°C	273.4 g
Distillate to 0 mbar, bath 80°C-95°C	531.6 g

- 25

GC analysis: (DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min ->280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

	Mass	Water content	Methacrylic acid	N-Methyl-methacryl amide	HB1r	Mass of product isolated
		[g]	[GC area%] 4.73 min	[GC area%] 5.986 min	[GC area%] 13.174 min	[g]
Distillate to 35 mbar	340.8	180	92.93	6.83		11.0
Distillate to 5 mbar	273.4	83	81.02	18.74	0.03	35.7
Distillate to 1 mbar	531.6	20	27.36	71.06	0.84	363.5
TOTAL						410.2

Without neutralization of the aqueous phase, after simple distillation, it is possible to isolate 410.2 g (67.3% of theory) of the product as a mixture with water and methacrylic acid, leaving around 230 g of solids. The distillates to 5 mbar and to 1 mbar (805 g, with 399 g of product) are fractionally distilled in Comparative Example 3.

5

Comparative Example 3: Distillation of N-methylmethacrylamide from aqueous methacrylic acid.

- 10 **Apparatus:** 1 l three-neck round-bottom flask, boiling capillary, 30 cm mirrored column with 6 x 6 Raschig rings, Liebig condenser, Claisen attachment, Thiele-Anschütz attachment, receiver, oil bath, vacuum pump

- 15 **Mixture:**
- | | |
|---------|--|
| 805 g | distillate from Comparative Example 2 |
| 66.5 mg | hydroquinone monomethyl ether (100 ppm) |
| 665 mg | octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (1000 ppm) |
| 33.3 mg | 2,4-dimethyl-6-tert-butylphenol (50 ppm) |

- 20 **Procedure:**

Time	Bath °C	Bottom °C	Top °C	Pressure mbar	Comment
00:00	20	12.0	20	0.52	start of heating
00:10	98	40.7	27	0.56	1st fraction
00:14	97	50.3	30	0.72	
00:19	93	60.8	32	2.0	solids content in liquid phase
00:25	96	68.4	52	1.1	
00:52	96	69.1	42	0.35	
01:22	112	72.3	37	0.20	2nd fraction, a lot of solids in liquid phase
01:36	113	73.4	38	0.21	significant bumping in the liquid phase, stopped

1st fraction 156.3 g

2nd fraction 48.5 g (cloudy distillate, "mini-lumps")

The liquid phase is filtered through a porcelain suction filter. Filtrate -> 292.5 g -> GC

- 25 A sample of the filtercake is dissolved in MeOH -> 307 g -> polymer.

GC analysis: (Meth. F241, DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min → 280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

	Mass	Water content [g]	Methacrylic acid [GC area%] 4.73 min	N-Methyl- methacrylamide [GC area%] 5.986 min	HB1 [GC area%] 13.174 min
1st fraction	156.3	103	99.887	0.083	
2nd fraction	48.5	-	99.616	0.320	
Liquid phase filtrate	292.5	-	64.559	35.100	0.049

- 5 While it was possible to very substantially isolate water and methacrylic acid, the product prepared with aqueous methylamine polymerizes, and so only around 25% N-methylmethacrylamide was present after distillation for 90 min.

10 **Comparative Example 4: Preparation of N-methylmethacrylamide from aqueous methylamine, workup by extraction**

Apparatus: analogous to Comparative Example 2

15 **Mixture:**

2.5	mol	F49 (18770-45, 96.61%; 1000 ppm S49)	= 398.9 g
2.5	mol	N-methylamine, 40% in H ₂ O	= 194.1 g
2.5	mol	ammonia, 25%	= 170 g

Theoretical yield: 247.8 g

20

Procedure: preparation of the crude product analogous to Comparative Example 2

The crude product is neutralized with NH₃ solution, with partial cooling. There was no phase separation.

- 25 The mixture is then extracted with MTBE (by GC only methacrylic acid present). This is followed by extraction 3 x with 300 ml each time of methyl methacrylate (MMA) and then again 3 x with 200 ml each time of MMA (4% product is still present in the last extract). The combined MMA phases are concentrated on a rotary evaporator under reduced pressure (bath temperature 60°C), with entrainment of H₂O still present.

- 30 **Yield:** 115.8 g

GC analysis: 20.4% methacrylic acid, 69.28% N-methylmethacrylamide

The water/methacrylic acid and N-methylmethacrylamide systems are very similar to one another.

Extraction can enable removal of the product only with great effort and poor yield.

5

Comparative example 5: Preparation of N-methylmethacrylamide by aqueous methylamine and neutralization of the residue with KOH

- 10 **Apparatus:** 2 l four-neck round-bottom flask with precision glass sabre stirrer, 500 ml dropping funnel, Pt-100 liquid phase thermometer, reflux condenser, ice bath

Mixture:

- 6.0 mol methacrylic anhydride = 938.1 g
 15 6.0 mol methylamine, 40% in H₂O = 465.9 g*

Theoretical yield: 594.8 g

Procedure: Methacrylic anhydride is initially charged and cooled to below 10°C. Then the metered addition of methylamine is started (exothermic reaction, cooling with ice/H₂O, slight mist formation).

- 20 Dropwise addition and cooling are effected such that the temperature does not rise above 10°C. After dropwise addition has ended, the mixture is stirred for a further 2 h for further reaction. The cooling is removed.

After storage overnight (mixture becomes pale yellow), the mixture is transferred to a 4 l flask and neutralized with 5.9 mol of KOH (50% in H₂O, addition via dropping funnel, cooling with H₂O bath,

- 25 addition of 2 drops of phenolphthalein solution) -> pH 6.5.

The precipitated solids are then filtered off with suction using a porcelain suction filter, and the filtrate is concentrated on a rotary evaporator under reduced pressure (bath up to 80°C, for pressure see below) with addition of 1000 ppm of octadecyl 3-(3,5-di-tert-butyl-4-

- 30 2,2,6,6-tetramethylpiperidinoxyl (rad.) (based on theoretical yield of N-methylmethacrylamide).

Residue on the suction filter 77.5 g (b)

Residue in the flask 1026.2 g (a)

GC analysis: (DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min ->280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

	Mass [g]	LB 1.09-1.20 min	Methacrylic acid [GC area%] 4.73 min	N-Methyl- methacryl amide [GC area%] 5.986 min	HB1 [GC area%] 13.174 min	Proportion of product in fraction [% by wt.]	Mass of product isolated [g]
Dist. to 60 mbar	316.4	1.081	6.121	89.158	1.113	7.0	22.15
Dist. to 1 mbar	163.8	1.110	8.088	90.161	0.090	94.5	154.05

LB = low boilers

5

To ascertain the mass of the product in the fraction, an exactly defined amount of dimethylaminopropylmethacrylamide is added and the exact mass is determined via the comparison of the integrals.

On neutralization of the aqueous phase with KOH, after distillation, it is possible to isolate only 144.9 g (29.6% of theory) of the product as a dilute aqueous solution.

Comparative example 6: Preparation of N-methylmethacrylamide by aqueous methylamine and neutralization of the residue with NaOH

15

Apparatus: 2 l four-neck round-bottom flask with precision glass sabre stirrer, 500 ml dropping funnel, Pt-100 liquid phase thermometer, reflux condenser, cooling bath

Mixture:

20 6.0 mol methacrylic anhydride = 938.1 g
 6.0 mol methylamine, 40% in H₂O = 465.9 g*

Theoretical yield: 594.8 g

25 **Procedure:** Methacrylic anhydride is initially charged and cooled to below 10°C. Then the metered addition of methylamine is started (exothermic reaction, cooling with ice/H₂O, slight mist formation). Dropwise addition and cooling are effected such that the temperature does not rise above 10°C. After dropwise addition has ended, stirring is continued for another 2 h for further reaction; the cooling is removed.

Subsequently, the mixture is transferred to a 4 l flask and neutralized with 5.9 mol of 50% NaOH in H₂O (236 g of NaOH, 236 g of H₂O*) by addition via dropping funnel while cooling with an H₂O bath and addition of 2 drops of phenolphthalein solution up to pH 6.5-pH 7.0.

The precipitated solids are filtered off using a porcelain suction filter -> very poor filtration since the solid is waxy.

Filtrate: 1634 g

For analysis, in a GC vial, 1.5 g of filtrate are admixed with an internal standard and this is used to determine the content of N-methylmethacrylamide:
Calculated product content by GC analysis: 36.4% ~ 99.9% of theory.

The filtrate is concentrated on a rotary evaporator under reduced pressure (1). The condensate condensed (frozen) on the condenser is thawed out overnight and, the next day, the residue flask is concentrated once again to dryness at bath temperature 80°C and 1 mbar (2). In the course of this, significant amounts of solids precipitate out. The distillates obtained are analysed by means of GC.

GC: (DB5, 30 m, Ø 0.25 mm, film thickness 0.25 µm, 50°C, 3 min isothermal, 14°C/min ->280°C, 8 min isothermal; det: 280°C, inj.: 250°C)

Sample	Mass [g]	Product content by GC (as described in CE5) [% by wt.]	Product mass [g]
Filtrate	1634	36.4	594.8
Distillate to 60 mbar	172.2	14.0	24.1
Distillate flask	7.5	79.3	6.0
thawed out from the condenser (1)	230.6	23.1	53.3
thawed out from the condenser (2)	129.2	47.7	61.6
Total distillates	539.5		144.9

On neutralization of the aqueous phase with NaOH, after distillation, it is possible to isolate only 144.9 g (24.4% of theory) of the product as a dilute aqueous solution.

CLAIMS

1. Process for preparing N-methyl(meth)acrylamide,
characterized in that
 - 5 a) (meth)acrylic anhydride is reacted with methylamine,
 - b) the methylamine has a water content of < 10% by weight,
 - c) the stoichiometry of (meth)acrylic anhydride:amine is less than 1:2.
2. Process according to Claim 1, characterized in that the water content of the methylamine is
10 less than 5% by weight, preferably less than 1% by weight and most preferably < 0.1% by weight.
3. Process according to Claim 1, characterized in that the water content after the end of
addition of all reactants is less than 10% by weight.
- 15 4. Process according to Claim 3, characterized in that the water content after the end of
addition of all reactants is less than 5% by weight, preferably less than 1% by weight and
most preferably < 0.1% by weight.
- 20 5. Process according to Claim 1, characterized in that the reaction is conducted in a polar
aprotic solvent.
6. Process according to Claim 1, characterized in that the methylamine is added as a pure
substance, in liquid or gaseous form.
- 25 7. Process according to Claim 1, characterized in that methylamine is added as a gas.
8. Process according to Claim 1, characterized in that the excess of the amine reacted to
(meth)acrylic anhydride is between 0.5 and 1.5.
- 30 9. Process according to Claims 1 to 8, characterized in that the (meth)acrylic acid by-product is
removed or separated by distillation.
10. Process according to Claims 1 to 9, characterized in that the (meth)acrylic anhydride is
35 reacted with methylamine at temperatures between -20°C and 100°C, preferably between
0°C and 80°C and more preferably between 20°C and 50°C.

11. Process according to Claims 1 to 10, characterized in that the (meth)acrylic anhydride is reacted with methylamine at an absolute pressure of 0.5 bar to 10 bar, preferably 1 bar to 5 bar.