Process for preparing N-alkyl(meth)acrylamides

The invention relates to a process for preparing N-alkyl(meth)acrylamides by reacting (meth)acrylic anhydride with corresponding alkylamines.

The preparation of N-alkyl(meth)acrylamides is known. The Ritter reaction has for a long time been employed for preparing amides from nitriles and substrates which can form carbenium ions, e.g. tertiary or secondary alcohols, in the presence of strong mineral acids. DE 3131096 utilizes this process. A disadvantage is that the acid, which also functions as solvent, has to be neutralized and large amounts of salts are thus obtained. Furthermore, the product contains interfering impurities such as methacrylamide.

DE 4027843 describes a continuous process for preparing N-substituted (meth)acrylamides by transesterification of alkyl esters of (meth)acrylic acid with aliphatic and aromatic amines. Although the reaction makes do without a catalyst, it is carried out under severe conditions at > 150° and a pressure of about 160 bar.

The process claimed in EP 2358664 for preparing N-isopropylmethacrylamide by reacting methacrylic anhydride with isopropylamine requires, in the preferred variant, the presence of an inert organic solvent, which is associated with a purification requirement for recycling. In the solvent-free variant, large quantities of heat are evolved and can lead to discoloration of the product.

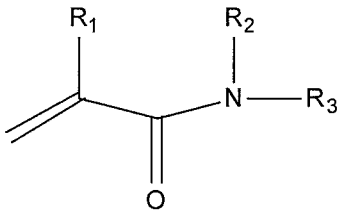
WO 2010/021956 discloses the preparation of N-alkyl(alkyl)acrylamides, likewise from the corresponding acid anhydride and alkylamine. The addition of the anhydride to the initially charged amine is claimed here. This process variant is likewise associated with strong evolution of heat, which can cause the discoloration cited above. In addition, there is only a narrow process window in which no severely troublesome lump formation occurs.

It is therefore an object of the present disclosure to provide an alternative process for preparing N-alkyl(meth)acrylamides which does not have the abovementioned

disadvantages and, in particular, produces products in high yield and purity, with these being obtained under moderate reaction conditions, preferably from 1 to 10 bar and from 20 to 100°C, and in a problem-free manner.

These objects and also further objects which are not set forth in detail but can readily be deduced or derived from the introductory presentation of the prior art are achieved by a process having the features defined herein. Advantageous modifications of the process of the disclosure are protected in the claims.

The disclosure provides a process for preparing N-alkyl(meth)acrylamides of the general formula (1),



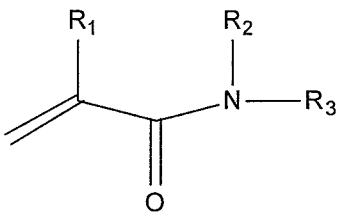
(1)

where R_1 is H or a CH_3 group, R_2 and R_3 are hydrogen or a linear, branched or cyclic alkyl radical or aryl radical having from 1 to 12 carbon atoms. The reaction is carried out by reacting initially charged (meth)acrylic anhydride with an aqueous solution of an alkylamine of the formula (2),

$$R_2R_3NH \quad (2)$$

where R_2 and R_3 are as defined above, and separating off the amide formed. The expression (meth)acrylic anhydride refers to both methacrylic anhydride and acrylic anhydride. It has surprisingly been found that this procedure does not lead, in contrast to WO 2010/021956, to uncontrolled precipitates in the form of lumps or deposits on the reactor wall at any point in time.

In one aspect of the present disclosure, there is provided a process for preparing N-alkyl(meth)acrylamides of the general formula (1),



(1)

where R_1 is H or a CH_3 group, R_2 and R_3 are hydrogen or a linear, branched or cyclic alkyl radical or aryl radical having from 1 to 12 carbon atoms and also reaction products of (meth)acrylic anhydride with amines from the group consisting of primary substituted aliphatic amines, benzylamine, allylamine, isomeric aminotoluenes, individually or in mixtures, isomeric xylidines, individually or in mixtures, which are substituted by one or more halogens, secondary aliphatic, cycloaliphatic or aromatic amines which are substituted by one or more halogens, dibenzylamine, morpholine, substituted piperidine,

characterized in that

initially charged (meth)acrylic anhydride is reacted with an aqueous solution of an alkylamine of the formula (2),

$$R_2R_3NH \quad (2)$$

where R_2 and R_3 are hydrogen or a linear, branched or cyclic alkyl radical or aryl radical having from 1 to 12 carbon atoms, or else amines from the group consisting of primary substituted aliphatic amines, benzylamine, allylamine, isomeric aminotoluenes, individually or in mixtures, isomeric xylidines, individually or in mixtures, which are substituted by one or more halogens, secondary aliphatic, cycloaliphatic or aromatic amines which are substituted by one or more halogens, dibenzylamine, morpholine, substituted piperidines, and the amide formed is separated off, the reaction is carried out from -5 °C to 40 °C at a pressure of from 0.5 to 6 bar, preferably at from 0 to 1 bar, where the addition of the aqueous amine solution to the (meth)acrylic anhydride is carried out at such a rate that the initial reaction temperature of the exothermic reaction does not rise above 25 °C, and the further introduction is carried out in such a way that the internal reactor temperature rises, as a result of the reaction, to a maximum value of 40 °C and the temperature of the cooling liquid used for cooling the reaction vessel is not below the crystallization temperature of the N-alkyl(meth)acrylamide in the reaction solution at any point in time.

Possible primary amines are primary, optionally substituted aliphatic amines, for

example methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dodecylamine, isopropylamine, isobutylamine and benzylamine and also allylamine and ammonia. Furthermore, it is possible to use primary cycloaliphatic amines, for example cyclopropylamine, cyclobutylamine, cyclopentylamine and cyclohexylamine. As primary aromatic amines, it is possible to use aniline, the isomeric aminotoluenes, either individually or in mixtures, and the

isomeric xylidines, either individually or in mixtures. These compounds can optionally be substituted by one or more halogens.

As secondary amines, it is likewise possible to use aliphatic, cycloaliphatic or aromatic amines which can optionally be substituted by one or more halogens. Particular preference is given to dimethylamine, diethylamine, methylethylamine, dibutylamine, dibenzylamine, morpholine and optionally substituted piperidines.

Since polymerizable compounds are prepared here, the reaction has to be carried out in the presence of polymerization inhibitors. The reaction can be carried out under atmospheric oxygen or protective gas. In the first case, the appropriate explosion protection limits have to be adhered to and inhibitors which act under atmospheric oxygen have to be used. Since the process of the disclosure preferably proceeds under protective gas, particularly preferably under nitrogen, only polymerization inhibitors which also act with exclusion of oxygen can be used in this case. As such polymerization inhibitors, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, N,N'-diphenyl-p-phenylenediamine, triazines, phenazines, phenothiazines, methylene blue or sterically hindered phenols, for example, are widely known in the art. These compounds can be used individually or in the form of mixtures and are generally commercially available. For further details, reference may be made to the relevant technical literature, in particular Römpp-Lexikon Chemie; editor: J. Falbe, M. Regitz; Stuttgart, New York; 10th edition (1996); keyword "Antioxidantien" [Antioxidants] and the literature references cited there. Particular preference is given to 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl or 4-methyl-2,6-di-tert-butylphenol, either individually or in mixtures. Customary concentrations used here are in the range from 1 to 2000 ppm, preferably from 20 to 200 ppm, particularly preferably from 40 to 80 ppm, based on the total reaction mixture.

In the process of the disclosure, the (meth)acrylic anhydride is placed in a suitable stirred reactor, optionally with external heat exchanger and circulation pump, admixed with polymerization inhibitors and cooled to below 30°C, preferably to from 10 to -5°C. The reactor is flushed with protective gas, preferably nitrogen. The aqueous solution of the amine is provided in a reservoir and likewise cooled to below 30°C, preferably to from 10 to -5°C. The concentration of the amine in the aqueous

solution can be from 50 to 90%, preferably from 60 to 80%, particularly preferably from 65 to 75%. The molar ratio of (meth)acrylic anhydride to amine is in the range from 0.8:1.2 to 1.2:0.8, preferably 1:1. The addition of the aqueous amine solution to the (meth)acrylic anhydride is carried out at such a rate that the initial reaction temperature of the exothermic reaction does not exceed 25°C, preferably does not exceed 15°C. The further addition is carried out in such a way that the internal temperature in the reactor increases, as a function of the conversion, to a maximum value of 40°C and the temperature of the cooling liquid used for cooling the reaction vessel is not below the crystallization temperature of the amine formed in the reaction solution at any point in time. The reactor pressure should be kept in the range from 0.5 to 6 bar, preferably from 0 to 1 bar.

For neutralization, the reaction solution is transferred to a further vessel, preferably equipped with a stirrer. Neutralization is carried out using alkaline solutions, preferably NaOH or KOH solution, particularly preferably ammonia solution. The reaction solution can optionally be diluted with water or the mother liquor from the centrifuge beforehand. Before commencement of neutralization, the reaction solution is cooled to below 20°C, preferably to below 15°C. The alkaline solution has to be introduced in such a way that the temperature does not exceed 60°C, preferably 50°C, at any point in time. After neutralization, the mixture with the precipitated product crystals is cooled to below 10°C, preferably to 5°C, particularly preferably to -5°C.

To isolate the solid from the neutralized mixture, it is possible to use solid/liquid separation methods with which a person skilled in the art will be familiar, e.g. filtration or centrifugation. In the process of the disclosure, preference is given to centrifugation with an optional preceding milling step. To mill the crystal suspension, it is possible to use, for example, suspension mills or wet mills (e.g. from Fryma). Centrifugation is carried out at temperatures below 10°C, preferably below 5°C, in particular below -5°C. The yield of N-akyl(meth)acrylamide is normally in the range from 80 to 85%, based on N-alkyl(meth)acrylic anhydride.

The following example illustrates the process of the disclosure, but does not restrict it in any way.

indicated, quality-reducing discoloration and decreases in yield occur. Similar problems arise when the appropriate amine is initially charged and (meth)acrylic anhydride is added thereto.

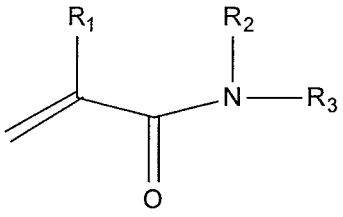
The N-alkyl(meth)acrylamides prepared by the process of the disclosure can be converted in a manner known per se into polymers and copolymers for use in a wide variety of applications.

List of reference numerals:

Number	Name
1	Stirred reactor
2	Pump
3	Metering pump
4	Reservoir vessel
5	Pump
6	Heat exchanger
7	Brine cooling
8	Stirred vessel
9	Buffer reservoir
10	Mill
11	Centrifuge
12	Pump

Claims

1. Process for preparing N-alkyl(meth)acrylamides of the general formula (1),



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where R_1 is H or a CH_3 group, R_2 and R_3 are hydrogen or a linear, branched or cyclic alkyl radical or aryl radical having from 1 to 12 carbon atoms and also reaction products of (meth)acrylic anhydride with amines from the group consisting of primary substituted aliphatic amines, benzylamine, allylamine, isomeric aminotoluenes, individually or in mixtures, isomeric xylidines, individually or in mixtures, which are substituted by one or more halogens, secondary aliphatic, cycloaliphatic or aromatic amines which are substituted by one or more halogens, dibenzylamine, morpholine, substituted piperidine,

characterized in that

initially charged (meth)acrylic anhydride is reacted with an aqueous solution of an alkylamine of the formula (2),

$$R_2R_3NH \qquad (2)$$

where R_2 and R_3 are hydrogen or a linear, branched or cyclic alkyl radical or aryl radical having from 1 to 12 carbon atoms, or else amines from the group consisting of primary substituted aliphatic amines, benzylamine, allylamine, isomeric aminotoluenes, individually or in mixtures, isomeric xylidines, individually or in mixtures, which are substituted by one or more halogens, secondary aliphatic, cycloaliphatic or aromatic amines which are substituted by one or more halogens, dibenzylamine, morpholine, substituted piperidines, and the amide formed is separated off, the reaction is carried out from -5 °C to 40 °C at a pressure of from 0.5 to 6 bar, preferably at from 0 to 1 bar, where the addition of the aqueous amine solution to the (meth)acrylic anhydride is carried out at

such a rate that the initial reaction temperature of the exothermic reaction does not rise above 25 °C, and the further introduction is carried out in such a way that the internal reactor temperature rises, as a result of the reaction, to a maximum value of 40 °C and the temperature of the cooling liquid used for cooling the reaction vessel is not below the crystallization temperature of the N-alkyl(meth)acrylamide in the reaction solution at any point in time.

2. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that reservoir and alkylamine are precooled to below 30°C, preferably to from 10 to -5°C, before the reaction.

3. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the resulting solution of N-alkyl(meth)acrylamide and (meth)acrylic acid is diluted with water, optionally with the centrifuge mother liquor, subsequently neutralized by means of an alkaline solution, preferably ammonia solution, NaOH or KOH, and the precipitated N-alkyl(meth)acrylamide is separated off.

4. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the reaction and also the neutralization and precipitation are each carried out in a separate vessel.

5. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the alkylamine to be reacted in the reaction is added in a 50-90% strength, preferably 60-80% strength, particularly preferably 65-75% strength, aqueous solution to the (meth)acrylic anhydride.

6. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the reaction is carried out in the presence of water-soluble polymerization inhibitors which act under inert gas, preferably nitrogen.

7. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the product crystal slurry is milled in a mill before being separated off in the centrifuge.

8. Process for preparing an N-alkyl(meth)acrylamide according to Claim 1, characterized in that the reactor is equipped with an external heat exchanger and a circulation pump.