in toluene and benzene, 1% to 5% by weight of azobisisobutyronitrile or benzoyl peroxide as radical initiator and of HBr into the first stirred reactor, maintained at a temperature of 10-30°C, with a residence time of 30 to 90 minutes. The reaction medium from the first reactor is withdrawn continuously and injected into an item of separation equipment heated to 65-80°C. The residual HBr released in the gas form is returned to the first reactor. The maximum yield indicated is 92.1%. This process requires a prolonged residence time for a moderate yield. Furthermore, the large amount of radical initiator can be the source of troublesome residues in the product.

All of these continuous processes operate with benzene, a carcinogenic and mutagenic solvent, and/or toluene, a solvent capable of producing benzyl bromide, a lachrymatory compound.

In point of fact, today the aim is increasingly to replace benzene and toluene with other solvents having a more favorable toxicity profile or generating less in the way of byproducts.

The patent EP 3 030 543 B1 provides a process for the continuous hydrobromination of 10-undecenoic acid which makes it possible to at least partially replace benzene with cyclohexane and/or methylcyclohexane. In this process, 10-undecenoic acid is reacted with HBr in liquid form. The document teaches that the implementation of the process in a countercurrent column with modification of solvent leads to a loss in yield, which can be compensated for when two successive reactors are used, the first with a turbulent flow and the second a laminar flow. This method exhibits the disadvantage of requiring an HBr in liquid form, which has the consequence of constraints in terms of HBr purity and considerable energy expenditures and capital costs in order to cool the HBr or an HBr solution to temperatures markedly below 0°C in order for the solubility of the HBr to be sufficient.

[**Summary**]

An aim of the disclosure is thus to provide a process for the continuous synthesis of ω-bromoalkanoic acids and esters by hydrobromination not employing benzene and/or toluene, which exhibits a satisfactory yield of product of formula (II), preferably of at least 92% and in particular of at least 94%.

According to one example, an aim of the disclosure is to provide a continuous synthesis process which saves energy, in particular requiring neither high pressure nor a temperature below 5°C.

According to another example, an aim of the disclosure is to provide a continuous synthesis process making possible the use of HBr contaminated with hydrogen, HCl or water.

According to another example, an aim of the disclosure is to provide a continuous synthesis process making it possible to reduce the amount of HBr introduced into the process, this compound being expensive to produce and to remove.

According to yet another example, an aim of the disclosure is to provide a continuous synthesis process with a reduced residence time, in particular of less than 30 minutes and very particularly of less than 15 minutes.

According to another example, an aim of the disclosure is to provide a continuous synthesis process making it possible to produce a compound of formula (II) comprising nothing or little in the way of impurities.

According to another example, an aim of the disclosure is to provide a continuous synthesis process not requiring solid radical initiators, which are reagents at risk of violent decomposition.

According to another example, an aim of the disclosure is a process for the production of aminocarboxylic acid or ester from a compound of formula (II).

Finally, according to another example, an aim of the disclosure is a process for the production of a polyamide or copolyamide from a compound of formula (II).

In point of fact, the present disclosure is based on the observation that it is possible to replace benzene and toluene, in the continuous production of ω-bromoalkanoic acids and esters by hydrobromination, with aliphatic solvents while maintaining a high yield under the condition of ensuring a sufficient molar excess of HBr during the reaction.

In order to obtain a high yield of compound of formula (II), it is important to properly control the thermal conditions because a high temperature promotes the appearance of entities not carrying bromine at the chain end.

Consequently, according to a first aspect, a subject matter of the disclosure is a process for the continuous synthesis of a compound of formula (II) $Br\text{-}(CH_2)_{n+2}\text{-}COOR$, comprising a stage consisting of:

(a) the hydrobromination of a compound of formula (I) $CH_2{=}CH\text{-}(CH_2)_n\text{-}COOR$:

where, in the formulae (I) and (II), n is an integer of between 7 and 9, and R is chosen from H or a linear or branched alkyl radical comprising from 1 to 10 carbon atoms, in particular methyl, ethyl, isopropyl or propyl,

with HBr in the presence of a radical initiator and of at least one solvent;

said process being characterized in that the reaction is carried out in the absence of benzene and of toluene and in that, in stage (a), the HBr is injected into the reaction mixture in the gaseous form and in stoichiometric excess.

Advantageously, the ratio of the molar flow rate of HBr injected in stage (a) to the molar flow rate of the compound of formula (I) injected in stage (a) is from 1.2 to 3, preferably from 1.3 to 2.2, more preferentially from 1.4 to 2 and in particular from 1.5 to 1.9.

According to one example, the outlet stream from the reactor of the liquid reaction mixture on conclusion of stage (a) comprises at least 2%, preferably at least 3%, and more preferentially at least 3.5% and in particular at least 4% by weight of HBr.

Preferably, the process of the disclosure additionally comprises the subsequent stages consisting of:

(b) the separation of the excess HBr from the liquid reaction mixture resulting from stage (a);

(b1) optionally, separation of the excess HBr from the gaseous reaction mixture resulting from stage (a); and

(c) the recycling of the HBr separated in stage (b) and (b1) if appropriate to stage (a).

Advantageously, the process of the disclosure comprises the stages consisting of:

(a1) introduction of the compound of formula (I), of the HBr, of the initiator and of the solvent(s) into a first reactor at an appropriate temperature for an appropriate residence time;

(a2) withdrawal of the reaction mixture from the first reactor and introduction into an item of separation equipment; if appropriate, followed by a subsequent stage of:

(b) separation of the residual HBr from the reaction mixture; and

(c) recycling of the separated HBr to stage (a1).

Stage (a) can be carried out in a reaction medium saturated with HBr. It can be carried out at a temperature of between 5 and 50°C, preferably between 10 and 40°C and very particularly from 20 to 30°C.

The radical initiator can be molecular oxygen used as is or as a mixture with inert gases, for example air or oxygen-enriched air.

The first reactor can in particular be a stirred vessel with a self-priming turbine or a jet loop reactor comprising a venturi. The item of separation equipment can in particular be a stirred vessel or a column.

Advantageously, the process according to the disclosure is carried out in the absence of aromatic solvent.

The product of formula (I) can be chosen from 11-bromoundecanoic acid, 10-bromodecanoic acid and 9-bromononanoic acid.

The solvent can be chosen from cyclohexane, methylcyclohexane, methylcyclopentane, n-hexane, 2-methylhexane, 3-methylhexane, n-heptane, isooctane, petroleum ether, tetralin, 1,1,1-trichloroethane, dibromoethane, chloroform, carbon tetrachloride, tetrachlorethylene, 1-bromopropane, dimethyl carbonate, tetrahydrofuran, 1,4 dioxane, 2-methyltetrahydrofuran, tetrahydropyran, 1-propoxypropane, 1-ethoxybutane, 2-isopropoxypropane, acetonitrile and their mixtures.

According to another aspect, the disclosure relates to a process for the synthesis of a compound of formula (III) NH_2-$(CH_2)_{n+2}$-COOR, comprising a stage consisting of:

(i) ammonolysis on the compound of formula (II) obtained by the above process; and

(ii) separation of the compound of formula (III) NH_2-$(CH_2)_{n+2}$-COOR formed.

Finally, according to another aspect, the disclosure relates to a process for the synthesis of a polyamide or copolyamide comprising the stage of polycondensation of the compound of formula (III) obtained by the above process, alone or as a mixture with other monomers.

[**Brief description of the figures**]

A better understanding of the invention will be obtained in the light of the description which follows and of the figures, which show:

Fig. 1: a diagram of an installation for the implementation of a process according to one embodiment of the invention;

Fig. 2: a diagram of an installation for the implementation of a process according to one embodiment of the invention comprising a venturi and an external heat exchanger;

Fig. 3: a diagram of an installation for the implementation of a process according to one embodiment of the invention comprising a venturi.

[**Description of the embodiments**]

Definition of the terms

In the context of the present disclosure, the term "**stoichiometric excess**, in the context of a continuous process," is understood to mean a greater molar flow rate of reactant than that required for the reaction envisaged. For example, one mole/hour of HBr is required to carry out the hydrobromination of one mole/hour of compound of formula (I). Consequently, a ratio of the molar flow rate of HBr/molar flow rate of the compound of formula (I) > 1 constitutes a stoichiometric excess of HBr.

In the context of the present disclosure, the term "**residence time**" is understood to mean the ratio of the volume occupied by the liquid reaction mixture to the sum of the flow rates by volume of compound of formula (I) and of solvents introduced into the process.

In the context of the present disclosure, the term "**ω-bromoalkanoic acids or esters**" is understood to denote alkanoic acids or esters carrying at least one bromine atom on the terminal carbon atom. ω-Alkanoic acids or esters having a linear chain are preferred.

The process of the invention is targeted at producing in particular ω-bromoalkanoic acids or esters of formula (II) below:

$$Br\text{-}(CH_2)_{n+2}\text{-}COOR \qquad (II)$$

in which n is an integer of between 7 and 9, and R is chosen from H or a linear or branched alkyl radical comprising from 1 to 10 carbon atoms, in particular methyl, ethyl, isopropyl or propyl.

The process is particularly advantageous for the manufacture of 12-bromododecanoic acid, 11-bromoundecanoic acid and 10-bromodecanoic acid.