preferably, at up to 235°C, most preferably at up to 230°C. In any case, a preferred lower temperature for the process of the present invention is 205°C, more preferably, 210°C, most preferably, 215°C. Preferred temperature ranges for the process of the present invention are between 205°C and up to 235°C, more preferably, between 210°C and 235°C.

Preferably, the reaction takes place at a temperature at which the reaction medium is in the liquid phase. Typically, the reaction medium is an aqueous solution.

Preferably, the base catalysed decarboxylation takes place with the dicarboxylic acid reactants and preferably the base catalyst in aqueous solution.

To maintain the reactants in the liquid phase under all above temperature conditions the decarboxylation reaction of the at least one dicarboxylic acid is carried out at suitable pressures in excess of atmospheric pressure. Suitable pressures which will maintain the reactants in the liquid phase in the above temperature ranges are greater than 225psia, more suitably, greater than 240psia, most suitably, greater than 260psia and in any case at a higher pressure than that below which the reactant medium will boil. There is no upper limit of pressure but the skilled person will operate within practical limits and within apparatus tolerances, for instance, at less than 10,000psia, more typically, at less than 5,000psia, most typically, at less than 4000 psia.

Preferably, the above reaction is at a pressure of between about 225 and 10000psia (15 to 680 bar). More preferably, the reaction is

diisocyanate, acrylonitrile, butadiene, butadiene and styrene (MBS) and ABS subject to any of the above comonomers not being the ~~momomer~~ monomer selected from methacrylic acid or a methacrylic acid ester in (i) or (ii) above in any given copolymerisation of the said acid monomer or ester in (i) or a said ester monomer in (ii) with one or more of the comonomers.

It is of course also possible to use mixtures of different comonomers. The comonomers themselves may or may not be prepared by the same process as the monomers from (i) or (ii) above.

According to a further aspect of the present invention there is provided polymethacrylic acid, polymethylmethacrylate (PMMA) and polybutylmethacrylate homopolymers or copolymers formed from the method of the second aspect of the invention herein.

According to a still further aspect of the present invention there is provided a process for the production of methacrylic acid or an ester thereof comprising:-
providing a source of a pre-acid selected from aconitic, citric and/or isocitric acid;
performing a decarboxylation and, if necessary, a dehydration step on the source of pre-acid by exposing the source thereof in the presence or absence of base catalyst to a sufficiently high temperature to provide itaconic, mesaconic and/or citraconic acid; and a process according to the first aspect of the present invention to provide methacrylic acid or an ester thereof.

By a source of aconitic, citric and/or isocitric acid is meant the acids and salts thereof such as group I or II metal salts thereof and includes solutions of the pre-acids and salts thereof, such as aqueous solutions thereof. Optionally, the salt may be acidified to liberate the free acid prior to, during or after the pre-acid decarboxylation step.

Preferably, the dicarboxylic acid(s) reactant(s) are exposed to the reaction conditions for a time period of at least 80 seconds.

Preferably, the dicarboxylic acid(s) reactant(s) or the source of pre-acids thereof of the present invention are exposed to the reaction conditions for a suitable time period to effect the required reaction, such as 80 seconds as defined herein but more preferably, for a time period of at least 100 seconds, yet more preferably at least about 120 seconds and most preferably at least about 150 seconds.

Typically, the dicarboxylic acid(s) reactant(s) or source of pre-acids thereof are exposed to the reaction conditions for a time period of less than about 2000 seconds, more typically less than about 1500 seconds, yet more typically less than about 1000 seconds.

Preferably, the dicarboxylic acid(s) reactant(s) or ~~the~~ a source of pre-acids thereof of the present invention are exposed to the reaction conditions for a time period of between about 75 seconds and 3000 seconds, more preferably between about 90 seconds and 2500 seconds and most preferably between about 120 seconds and 2000 seconds.

reactant medium will boil. There is no upper limit of pressure but the skilled person will operate within practical limits and within apparatus tolerances, for instance, at less than 10,000psia, more typically, at less than 5,000psia, most typically, at less than 4000 psia.

Preferably, the source of pre-acid decomposition reaction is at a pressure of between about 15 and 10000psia (1 and 680 bar). More preferably, the reaction is at a pressure of between about 20 and 5000 psia and yet more preferably between about 25 and 3000psia.

In a preferred embodiment, the source of pre-acid decomposition reaction is at a pressure at which the reaction medium is in the liquid phase.

Preferably, the source of pre-acid decomposition reaction is at a temperature and pressure at which the aqueous reaction medium is in the liquid phase.

All of the features contained herein may be combined with any of the above aspects, in any combination.

For a better understanding of the invention, and to show how embodiments of the same may be carried into effect, reference will now be made, by way of example, to the following examples.

Examples

A series of experiments were conducted investigating the decomposition of itaconic, citraconic and mesaconic acids to form methacrylic acid at various temperatures and residence times.

point range of 100-104°C was collected. The solid residue after distillation was orange/brown in colour. The total weight of the distillate was 512g. A small sample was taken for GC analysis.

The remaining aqueous distillate was placed into a 1L flask (weight added = 497g) and toluene was added (500g). The resultant bi-phasic mixture was then shaken rapidly for five minutes and then left to stand overnight. The two phases were then separated.

The organic phase was then analysed by GC, this indicated that the organic liquid was 3.1% MAA and 96.9% Toluene. Based upon the weight% MAA in the organic extract 16.1g of MAA was transferred into the organic phase. Purification is completed by removal of the toluene employing reduced pressure distillation.

~~Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.~~

~~All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.~~

~~Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same,~~

~~equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.~~

~~The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.~~

Claims

1. A process for the production of methacrylic acid or esters thereof by the base catalysed decarboxylation of at least one dicarboxylic acid selected from itaconic, citraconic or mesaconic acid or mixtures thereof in an aqueous reaction medium, wherein the decarboxylation is carried out at a temperature in the range from 200°C and up to 239°C and wherein the methacrylic acid is isolated from the aqueous reaction medium by a purification process which does not include introducing an organic solvent to the said aqueous reaction medium for solvent extraction of the methacrylic acid into an organic phase.

2. A method or process according to any claim 1, wherein the dicarboxylic acid(s) reactant(s) or ~~the~~ a source of pre-acids thereof are exposed to the reaction conditions for a time period of between ~~about~~ 75 seconds and 3000 seconds.

3. A process for the production of methacrylic acid by the base catalysed decarboxylation of at least one dicarboxylic acid selected from itaconic, citraconic or mesaconic acid or mixtures thereof, wherein the decarboxylation is carried out in the temperature range between 200 and 239°C and the dicarboxylic acid(s) reactant(s) are exposed to the reaction conditions for a time period of at least 80 seconds.

4. A process according to any preceding claim, wherein the decarboxylation reaction is carried

out at a pressure of between ~~about 225 and 10000 psia~~ 15 and 680 bar.

5. A process according to claims 1, 2 or 4, wherein suitable processes to isolate the methacrylic acid from the aqueous reaction medium are selected from distillation and fractional crystallisation wherein crystallisation can include crystallisation of the free acid or crystallisation of a salt of the acid such as the group I and II metal salt, for example the calcium salt, followed by acidification to regenerate the free MAA, wherein crystallisation may be preceded by suitable separation such as ion exchange chromatography, wherein crystallisation may include bipolar membrane electrodialysis (BPMED) to increase the purity of the MAA prior to crystallisation, for example by forming MAA and NaOH from sodium methacrylate, and wherein the isolation technique may involve esterification to the alkyl ester followed by distillation and optional subsequent hydrolysis to regenerate the MAA.

6. A process according to any preceding claim, wherein the catalyst comprises a source of OH^- ions.

7. A process according to any preceding claim, wherein the base catalyst is selected from the group consisting of a metal oxide, hydroxide, carbonate, acetate (ethanoate), alkoxide, hydrogencarbonate; or salt of a decomposable di- or tri-carboxylic acid; or a quaternary ammonium

$Ba(RCO_2)_2$, where RCO_2 is selected from itaconate, citrate, oxalate, methacrylate; $(NH_4)_2(CO_2RCO_2)$, $Na_2(CO_2RCO_2)$, $K_2(CO_2RCO_2)$, $Rb_2(CO_2RCO_2)$, $Cs_2(CO_2RCO_2)$, $Mg(CO_2RCO_2)$, $Ca(CO_2RCO_2)$, $(NH_4)_2(CO_2RCO_2)$, where CO_2RCO_2 is selected from mesaconate, citraconate, itaconate, oxalate; $(NH_4)_3(CO_2R(CO2)CO_2)$, $Na_3(CO_2R(CO2)CO_2)$, $K_3(CO_2R(CO_2)CO_2)$, $Rb_3(CO_2R(CO_2)CO_2)$, $Cs_3(CO_2R(CO_2)CO_2)$, $Mg_3(CO_2R(CO_2)CO_2)_2$, $Ca_3(CO_2R(CO_2)CO_2)_2$, $(NH_4)_3(CO_2R(CO_2)CO_2)$, where $CO_2R(CO_2)CO_2$ is selected from citrate, isocitrate; and tetramethylammonium hydroxide.

9. A process according to any preceding claim, wherein the effective mole ratio of base OH^-:acid is between 0.001-2:1.

10. A process according to any preceding claim, wherein the concentration of the dicarboxylic acid reactant(s) is in the range 0.05M-20M.

11. A process according to any preceding claim, wherein the concentration of the catalyst in the reaction mixture (including the decomposition of the source of pre-acid mixture) is at least 0.1M.

12. A process according to any preceding claim, wherein the concentration of the catalyst in the reaction mixture (including the decomposition of the source of pre-acid mixture) is less than about 10M.

13. A process according to any preceding claim, wherein the reaction pH is between ~~about~~ 2 and 9.

14. A process for the production of methacrylic acid or an ester thereof comprising:- providing a source of a pre-acid selected from aconitic, citric and/or isocitric acid; performing a decarboxylation and, if necessary, a dehydration step on the source of pre-acid by exposing the source thereof in the presence or absence of base catalyst to a ~~sufficiently high~~ temperature to provide itaconic, mesaconic and/or citraconic acid; and a process according to claims 1 to 13 to provide methacrylic acid or an ester thereof.

15. A process according to claim 14, wherein the temperature ranges for the source of pre-acid decomposition are between 110 and up to 349°C.

16. A process according to claim 14 or 15, wherein the pre-acid decomposition reaction is at a pressure of between ~~about 15 and 10000psia~~ 1 and 680 bar.

17. A method of preparing polymers or copolymers of methacrylic acid or methacrylic acid esters, comprising the steps of

(i) preparation of methacrylic acid or ester thereof in accordance with the process of claims 1 to 16;
(ii) optional esterification of the methacrylic acid prepared in (i) to produce the methacrylic acid ester;
(iii) polymerisation of the methacrylic acid or ester thereof prepared in (i) and/or the ester prepared in (ii), optionally with one or more

comonomers not being the ~~momomer~~ monomer selected from methacrylic acid or a methacrylic acid ester in (i) or (ii) above in any given copolymerisation of the said acid monomer or ester in (i) or a said ester monomer in (ii) with one or more of the comonomers.

21. A method according to any of claims 1-13 or 17-20, wherein the itaconic, citraconic or mesaconic acids are produced from a source of pre-acids.

~~22. A process for the production of methacrylic acid as described herein and with reference to any one or more examples.~~

~~23. A method of preparing polymer or copolymers as described herein.~~