

A PROCESS FOR THE PRODUCTION OF METHACRYLIC ACID AND ITS
DERIVATIVES AND POLYMERS PRODUCED THEREFROM

The present invention relates to a process for the
5 production of methacrylic acid or derivatives such as
esters thereof by the decarboxylation of itaconic acid or a
source thereof in the presence of base catalysts, in
particular, but not exclusively, a process for the
production of methacrylic acid or methyl methacrylate.

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Methacrylic acid (MAA) and its methyl ester, methyl
methacrylate (MMA) are important monomers in the chemical
industry. Their main application is in the production of
plastics for various applications. The most significant
15 polymerisation application is the casting, moulding or
extrusion of polymethyl methacrylate (PMMA) to produce high
optical clarity plastics. In addition, many copolymers are
used, important copolymers are copolymers of methyl
methacrylate with α -methyl styrene, ethyl acrylate and
20 butyl acrylate. Currently MMA (and MAA) is produced
entirely from petrochemical feedstocks.

Conventionally, MMA has been produced industrially via the
so-called acetone-cyanohydrin route. The process is capital
25 intensive and produces MMA from acetone and hydrogen
cyanide at a relatively high cost. The process is effected
by forming acetone cyanohydrin from the acetone and
hydrogen cyanide: dehydration of this intermediate yields
methacrylamide sulphate, which is then hydrolysed to
30 produce MAA. The intermediate cyanohydrin is converted with
sulphuric acid to a sulphate ester of the methacrylamide,
methanolysis of which gives ammonium bisulphate and MMA.

However, this method is not only expensive, but both sulphuric acid and hydrogen cyanide require careful and expensive handling to maintain a safe operation and the process produces large amounts of ammonium sulphate as a by-product. Conversion of this ammonium sulphate either to a useable fertilizer or back to sulphuric acid requires high capital cost equipment and significant energy costs.

Alternatively, in a further process, it is known to start with an isobutylene or, equivalently, t-butanol reactant which is then oxidized to methacrolein and then to MAA.

An improved process that gives a high yield and selectivity and far fewer by-products is a two stage process known as the Alpha process. Stage I is described in WO96/19434 and relates to the use of 1,2-bis-(di-t-butylphosphinomethyl)benzene ligand in the palladium catalysed carbonylation of ethylene to methyl propionate in high yield and selectivity. The applicant has also developed a process for the catalytic conversion of methyl propionate (MEP) to MMA using formaldehyde. A suitable catalyst for this is a caesium catalyst on a support, for instance, silica. This two stage process although significantly advantageous over the competitive processes available still nevertheless relies on ethylene feed stocks predominantly from crude oil and natural gas, albeit bioethanol is also available as a source of ethylene.

For many years, biomass has been offered as an alternative to fossil fuels both as a potential alternative energy resource and as an alternative resource for chemical process feedstocks. Accordingly, one obvious solution to

the reliance on fossil fuels is to carry out any of the known processes for the production of MMA or MAA using a biomass derived feedstock.

- 5 In this regard, it is well known that syngas (carbon monoxide and hydrogen) can be derived from Biomass and that methanol can be made from syngas. Several Industrial plants produce methanol from syngas on this basis, for example, at Lausitzer Analytik GmbH Laboratorium für Umwelt und
10 Brennstoffe Schwarze Pumpe in Germany and Biomethanol Chemie Holdings, Delfzijl, Netherlands. Nouri and Tillman, Evaluating synthesis gas based biomass to plastics (BTP) technologies, (ESA-Report 2005:8 ISSN 1404-8167) teach the viability of using methanol produced from synthesis gas as
15 a direct feedstock or for the production of other feedstocks such as formaldehyde. There are also many patent and non-patent publications on production of syngas suitable for production of chemicals from biomass.
- 20 The production of ethylene by dehydration of biomass derived ethanol is also well established with manufacturing plants in, especially, Brazil.

The production of propionic acid from carbonylation of
25 ethanol and the conversion of biomass derived glycerol to molecules such as acrolein and acrylic acid is also well established in the patent literature.

Thus ethylene, carbon monoxide and methanol have well
30 established manufacturing routes from biomass. The chemicals produced by this process are either sold to the

same specification as oil/gas derived materials, or are used in processes where the same purity is required.

Thus in principle there is no barrier to operation of the
5 so called Alpha process above to produce methyl propionate from Biomass derived feedstocks. In fact, its use of simple feedstocks such as ethylene, carbon monoxide and methanol rather sets it apart as an ideal candidate.

10 In this regard, WO2010/058119 relates explicitly to the use of biomass feedstocks for the above Alpha process and the catalytic conversion of methyl propionate (MEP) produced to MMA using formaldehyde. These MEP and formaldehyde feedstocks could come from a biomass source as mentioned
15 above. However, such a solution still involves considerable processing and purification of the biomass resource to obtain the feedstock which processing steps themselves involve the considerable use of fossil fuels.

20 Further, the Alpha process requires multiple feedstocks in one location which can lead to availability issues. It would therefore be advantageous if any biochemical route avoided multiple feedstocks or lowered the number of feedstocks.

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Therefore, an improved alternative non-fossil fuel based route to acrylate monomers such as MMA and MAA is still required.

30 PCT/GB2010/052176 discloses a process for the manufacture of aqueous solutions of acrylates and methacrylates

respectively from solutions of malate and citramalate acids and their salts.

Carlsson et al., Ind. Eng. Chem. Res. 1994, 33, 1989-1996 has disclosed itaconic acid decarboxylation to MAA at high
5 temperatures of 360°C and with a maximum yield of 70%. Carlsson found a decrease in selectivity in moving from 360 to 350°C under ideal conditions.

Generally, for industrial processes a high selectivity is
10 required to avoid generation of unwanted by-products which would eventually render a continuous process untenable. For this purpose, particularly for a continuous process, selectivity for the desired product should exceed 90%.

15 Surprisingly, it has now been discovered that high selectivity to MAA formation in excess of 90% in the decarboxylation of itaconic acid and other itaconic equilibrated acids can be achieved at significantly lower temperatures.

20 According to a first aspect of the present invention there is provided a process for the production of methacrylic acid by the base catalysed decarboxylation of at least one dicarboxylic acid selected from itaconic, citraconic or
25 mesaconic acid or mixtures thereof, wherein the decarboxylation is carried out at a temperature in the range from 100 to 199°C.

The dicarboxylic acid(s) reactants and the base catalyst
30 need not necessarily be the only compounds present. The dicarboxylic acid(s) together with any other compounds

present are generally dissolved in an aqueous solution for the base catalysed thermal decarboxylation.

Advantageously, carrying out the decarboxylation at lower
5 temperatures prevents the production of significant amounts of by-products which may be difficult to remove and may cause further purification and processing problems in an industrial process. Therefore, the process provides a surprisingly improved selectivity in this temperature
10 range. Furthermore, lower temperature decarboxylation uses less energy and thereby creates a smaller carbon footprint than high temperature decarboxylations.

The dicarboxylic acids are available from non-fossil fuel
15 sources. For instance, the itaconic, citraconic or mesaconic acids could be produced from a source of pre-acids such as citric acid or isocitric acid by dehydration and decarboxylation at suitably high temperatures or from aconitic acid by decarboxylation at suitably high
20 temperatures. It will be appreciated that a base catalyst is already present so that the source of pre-acid dehydration and/or decomposition may potentially be base catalysed under such suitable conditions. Citric acid and isocitric acid may themselves be produced from known
25 fermentation processes and aconitic acid may be produced from the former acids. Accordingly, the process of the invention may provide a biological or substantially biological route to generate methacrylates directly whilst minimising reliance on fossil fuels.

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As detailed above, the base catalysed decarboxylation of the at least one dicarboxylic acid takes place at less than

200°C, more typically, at less than 190°C, more preferably, at up to 195°C, most preferably at up to 185°C. In any case, a preferred lower temperature for the process of the present invention is 110°C, more preferably, 120°C, most
5 preferably, 130°C. Preferred temperature ranges for the process of the present invention are between 110°C and up to 190°C, more preferably, between 115°C and 185°C, most preferably, between 125°C and 180°C.

10 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
15 with the dicarboxylic acid reactants and preferably the base catalyst in aqueous solution.

To maintain the reactants in the liquid phase under all the above temperature conditions the decarboxylation reaction
20 of the at least one dicarboxylic acid is carried out at suitable pressures at or in excess of atmospheric pressure. Suitable pressures which will maintain the reactants in the liquid phase in the above temperature ranges are greater than 20psia, more suitably, greater than 25psia, most
25 suitably, greater than 35psia 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
30 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 20 and 10000psia. More preferably, the reaction is at a pressure of between about 25 and 5000 psia and yet more preferably between about 35 and 3000psia.

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In a preferred embodiment, the above reaction is at a pressure at which the reaction medium is in the liquid phase.

- 10 Preferably, the reaction is at a temperature and pressure at which the reaction medium is in the liquid phase.

As mentioned above, the catalyst is a base catalyst.

- 15 Preferably, the catalyst comprises a source of OH^- ions. Preferably, 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
20 ammonium compound of one of the above; or one or more amines; more preferably a Group I or Group II metal oxide, hydroxide, carbonate, acetate, alkoxide, hydrogencarbonate or salt of a di- or tri-carboxylic acid or methacrylic acid.

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- Preferably, the base catalyst is selected from one or more of the following: LiOH , NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, CsOH , $\text{Sr}(\text{OH})_2$, RbOH , NH_4OH , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , MgCO_3 , CaCO_3 , SrCO_3 , BaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, LiHCO_3 ,
30 NaHCO_3 , KHCO_3 , RbHCO_3 , CsHCO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, $\text{Sr}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$, NH_4HCO_3 , Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , BaO , $\text{Li}(\text{OR}^1)$, $\text{Na}(\text{OR}^1)$, $\text{K}(\text{OR}^1)$, $\text{Rb}(\text{OR}^1)$, $\text{Cs}(\text{OR}^1)$,

$\text{Mg}(\text{OR}^1)_2$, $\text{Ca}(\text{OR}^1)_2$, $\text{Sr}(\text{OR}^1)_2$, $\text{Ba}(\text{OR}^1)_2$, $\text{NH}_4(\text{OR}^1)$ where R^1 is any C_1 to C_6 branched, unbranched or cyclic alkyl group, being optionally substituted with one or more functional groups; $\text{NH}_4(\text{RCO}_2)$, $\text{Li}(\text{RCO}_2)$, $\text{Na}(\text{RCO}_2)$, $\text{K}(\text{RCO}_2)$, $\text{Rb}(\text{RCO}_2)$,
5 $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$, $\text{Ca}(\text{RCO}_2)_2$, $\text{Sr}(\text{RCO}_2)_2$ or $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is selected from, mesaconate, citraconate, itaconate, citrate, oxalate and methacrylate; $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, $\text{Li}_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$, $\text{K}_2(\text{CO}_2\text{RCO}_2)$, $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$, $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$, $\text{Mg}(\text{CO}_2\text{RCO}_2)_2$, $\text{Ca}(\text{CO}_2\text{RCO}_2)_2$, $\text{Sr}(\text{CO}_2\text{RCO}_2)_2$,
10 $\text{Ba}(\text{CO}_2\text{RCO}_2)_2$, $(\text{NH}_4)_3(\text{CO}_2\text{RCO}_2)_3$, where CO_2RCO_2 is selected from mesaconate, citraconate, itaconate and oxalate; $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Li}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $\text{Sr}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$,
15 $\text{Ba}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$, where $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is selected from citrate, isocitrate and aconitate; methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, cyclohexylamine, aniline; and R_4NOH where R is selected from methyl, ethyl propyl, butyl. More preferably, the base is selected from one or more of the following: LiOH , NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, CsOH , $\text{Sr}(\text{OH})_2$, RbOH , NH_4OH , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , MgCO_3 , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, LiHCO_3 , NaHCO_3 , KHCO_3 , RbHCO_3 , CsHCO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, $\text{Sr}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$, NH_4HCO_3 , Li_2O ,
20 Na_2O , K_2O , Rb_2O , Cs_2O ; $\text{NH}_4(\text{RCO}_2)$, $\text{Li}(\text{RCO}_2)$, $\text{Na}(\text{RCO}_2)$, $\text{K}(\text{RCO}_2)$, $\text{Rb}(\text{RCO}_2)$, $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$, $\text{Ca}(\text{RCO}_2)_2$, $\text{Sr}(\text{RCO}_2)_2$ or $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is selected from itaconate, citrate, oxalate, methacrylate; $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, $\text{Li}_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$, $\text{K}_2(\text{CO}_2\text{RCO}_2)$, $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$, $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$,
25 $\text{Mg}(\text{CO}_2\text{RCO}_2)_2$, $\text{Ca}(\text{CO}_2\text{RCO}_2)_2$, $\text{Sr}(\text{CO}_2\text{RCO}_2)_2$, $\text{Ba}(\text{CO}_2\text{RCO}_2)_2$, $(\text{NH}_4)_3(\text{CO}_2\text{RCO}_2)_3$, where CO_2RCO_2 is selected from, mesaconate, citraconate, itaconate, oxalate; $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_3$,

$\text{Li}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $\text{Sr}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $\text{Ba}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, where $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is selected from
5 citrate, isocitrate; tetramethylammonium hydroxide and
tetraethylammonium hydroxide. Most preferably, the base is
selected from one or more of the following: NaOH , KOH ,
 $\text{Ca}(\text{OH})_2$, CsOH , RbOH , NH_4OH , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 ,
 MgCO_3 , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, $\text{NH}_4(\text{RCO}_2)$, $\text{Na}(\text{RCO}_2)$, $\text{K}(\text{RCO}_2)$,
10 $\text{Rb}(\text{RCO}_2)$, $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$, $\text{Ca}(\text{RCO}_2)_2$, $\text{Sr}(\text{RCO}_2)_2$ or
 $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is selected from itaconate, citrate,
oxalate, methacrylate; $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$,
 $\text{K}_2(\text{CO}_2\text{RCO}_2)$, $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$, $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$, $\text{Mg}(\text{CO}_2\text{RCO}_2)$,
 $\text{Ca}(\text{CO}_2\text{RCO}_2)$, $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, where CO_2RCO_2 is selected from
15 mesaconate, citraconate, itaconate, oxalate;
 $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, where $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is
selected from citrate, isocitrate; and tetramethylammonium
20 hydroxide.

The catalyst may be homogeneous or heterogeneous. In one
embodiment, the catalyst may be dissolved in the liquid
reaction phase. However, the catalyst may be suspended on
25 a solid support over which the reaction phase may pass. In
this scenario, the reaction phase is preferably maintained
in a liquid, more preferably, an aqueous phase.

Preferably, the effective mole ratio of base OH^- :acid is
30 between 0.001-2:1, more preferably, 0.01-1.2:1, most
preferably, 0.1-1:1, especially, 0.3-1:1. By the effective

mole ratio of base OH^- is meant the nominal molar content of OH^- derived from the compounds concerned.

By acid is meant the moles of acid. Thus, in the case of a
5 monobasic base, the effective mole ratios of base OH^- :acid will coincide with those of the compounds concerned but in the case of di or tribasic bases the effective mole ratio will not coincide with that of mole ratio of the compounds concerned.

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Specifically, this may be regarded as the mole ratio of monobasic base: di or tri carboxylic acid is preferably between 0.001-2:1, more preferably, 0.01-1.2:1, most preferably, 0.1-1:1, especially, 0.3-1:1.

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As the deprotonation of the acid to form the salt is only referring to a first acid deprotonation in the present invention, in the case of di or tribasic bases, the mole ratio of base above will vary accordingly.

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Optionally, the methacrylic acid product may be esterified to produce an ester thereof. Potential esters may be selected from C_1 - C_{12} alkyl or C_2 - C_{12} hydroxyalkyl, glycidyl, isobornyl, dimethylaminoethyl, tripropyleneglycol esters.

25 Most preferably the alcohols or alkenes used for forming the esters may be derived from bio sources, e.g. biomethanol, bioethanol, biobutanol.

According to a second aspect of the present invention there
30 is provided a method of preparing polymers or copolymers of methacrylic acid or methacrylic acid esters, comprising the steps of

(i) preparation of methacrylic acid in accordance with the first aspect of the present invention;

(ii) optional esterification of the methacrylic acid prepared in (i) to produce the methacrylic acid ester;

(iii) polymerisation of the methacrylic acid prepared in (i) and/or the ester prepared in (ii), optionally with one or more comonomers, to produce polymers or copolymers thereof.

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Preferably, the methacrylic acid ester of (ii) above is selected from C₁-C₁₂ alkyl or C₂-C₁₂ hydroxyalkyl, glycidyl, isobornyl, dimethylaminoethyl, tripropyleneglycol esters, more preferably, ethyl, n-butyl, i-butyl, hydroxymethyl, hydroxypropyl or methyl methacrylate, most preferably, methyl methacrylate, ethyl acrylate, butyl methacrylate or butyl acrylate.

Advantageously, such polymers will have an appreciable portion if not all of the monomer residues derived from a source other than fossil fuels.

In any case, preferred comonomers include for example, monoethylenically unsaturated carboxylic acids and dicarboxylic acids and their derivatives, such as esters, amides and anhydrides.

Particularly preferred comonomers are acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, iso-bornyl acrylate, methacrylic acid, methyl methacrylate, ethyl

methacrylate, propyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, lauryl methacrylate, glycidyl methacrylate, hydroxypropyl methacrylate, iso-bornyl methacrylate, dimethylaminoethyl methacrylate, tripropyleneglycol diacrylate, styrene, α -methyl styrene, vinyl acetate, isocyanates including toluene diisocyanate and p,p'-methylene diphenyl diisocyanate, acrylonitrile, butadiene, butadiene and styrene (MBS) and ABS subject to any of the above comonomers not being the monomer selected from methacrylic acid or a methacrylic acid ester in (i) or (ii) above in any given copolymerisation of the said acid monomer 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 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, 5 mesaconic and/or citraconic acid; and a process according to the first aspect of the present invention to provide methacrylic acid.

By a source of aconitic, citric and/or isocitric acid is 10 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 15 step.

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

20 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 25 at least 100 seconds, yet more preferably at least about 120 seconds and most preferably at least about 240 seconds.

Typically, the dicarboxylic acid(s) reactant(s) or source 30 of pre-acids thereof are exposed to the reaction conditions for a time period of less than about 85000 seconds, more

typically less than about 30000 seconds, yet more typically less than about 10000 seconds.

Preferably, the dicarboxylic acid(s) reactant(s) or the
5 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 90000 seconds, more preferably between about 90 seconds and 35000 seconds and most preferably between about 120 seconds and 10000 seconds.

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Therefore, according to a further aspect of the present invention there is provided a process for the production of methacrylic acid by the base catalysed decarboxylation of at least one dicarboxylic acid selected from itaconic,
15 citraconic or mesaconic acid or mixtures thereof, wherein the decarboxylation is carried out in the temperature range between 100 and 199°C and the dicarboxylic acid(s) reactant(s) are exposed to the reaction conditions for a time period of at least 80 seconds.

20

Advantageously, in this temperature range high selectivities can be achieved at residence times sufficient to allow heating of the reactants in the reaction medium.

25 Preferably, the dicarboxylic acid(s) reactant(s) or the source of pre-acids thereof of the present invention are dissolved in water so that the reaction occurs under aqueous conditions.

30 It will be clear from the way in which the above reactions are defined that if the source of pre-acid is decarboxylated and, if necessary, dehydrated in a reaction

medium then the reaction medium may simultaneously be effecting base catalysed decarboxylation of the at least one dicarboxylic acid selected from itaconic, citraconic or mesaconic acid or mixtures thereof produced from the source of pre-acid according to the first aspect of the invention. Accordingly, the decarboxylation and if necessary, dehydration of the source of pre-acid and the base catalysed decarboxylation of the at least one dicarboxylic acid may take place in one reaction medium i.e. the two processes may take place as a so called "one pot" process. However, it is preferred that the source of pre-acid is decarboxylated and, if necessary, dehydrated substantially without base catalysis so that the decarboxylation and if necessary, dehydration of the source of pre-acid and the base catalysed decarboxylation of the at least one dicarboxylic acid take place in separate steps.

Preferably, the concentration of the dicarboxylic acid reactant(s) is at least 0.1M, preferably in an aqueous source thereof; more preferably at least about 0.2M, preferably in an aqueous source thereof; most preferably at least about 0.3M, preferably in an aqueous source thereof, especially, at least about 0.5M. Generally, the aqueous source is an aqueous solution.

Preferably, the concentration of the dicarboxylic acid reactant(s) is less than about 10M, more preferably, less than 8M, preferably in an aqueous source thereof; more preferably, less than about 5M, preferably in an aqueous source thereof; more preferably less than about 3M, preferably in an aqueous source thereof.

Preferably, the concentration of the dicarboxylic acid reactant(s) is in the range 0.05M-20, typically, 0.05-10M, more preferably, 0.1M-5M, most preferably, 0.3M-3M.

5 The base catalyst may be dissolvable in a liquid medium, which may be water or the base catalyst may be heterogeneous. The base catalyst may be dissolvable in the reaction mixture so that reaction is effected by exposing the reactants to the temperatures given herein which are
10 temperatures in excess of that at which base catalysed decarboxylation of the reactant(s) to methacrylic acid and/or the source of pre-acids to the dicarboxylic acids will occur. The catalyst may be in an aqueous solution. Accordingly, the catalyst may be homogenous or
15 heterogeneous but is typically homogenous. Preferably, the concentration of the catalyst in the reaction mixture (including the decomposition of the source of pre-acid mixture) is at least 0.1M or greater, preferably in an aqueous source thereof; more preferably at least about
20 0.2M, preferably in an aqueous source thereof; more preferably at least about 0.3M.

Preferably, the concentration of the catalyst in the reaction mixture (including the decomposition of the source
25 of pre-acid mixture) is less than about 10M, more preferably, less than about 5M, more preferably less than about 2M and, in any case, preferably less than or equal to that which would amount to a saturated solution at the temperature and pressure of the reaction.

30

Preferably, the mole concentration of OH^- in the aqueous reaction medium or optionally source of pre-acid

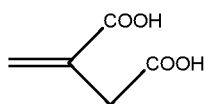
decomposition is in the range 0.05M-20M, more preferably, 0.1-5M, most preferably, 0.2M-3M.

Preferably, the reaction conditions are weakly acidic.

- 5 Preferably, the reaction pH is between about 2 and 9, more preferably between about 3 and about 6.

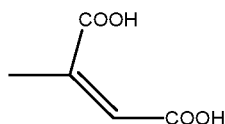
For the avoidance of doubt, by the term itaconic acid, it is meant the following compound of formula (i)

10



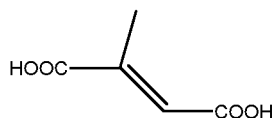
(i)

- 15 For the avoidance of doubt, by the term citraconic acid, it is meant the following compound of formula (ii)



20 (ii)

- For the avoidance of doubt, by the term mesaconic acid, it is meant the following compound of formula (iii)
- 25



(iii)

As mentioned above, the process of the present invention may be homogenous or heterogeneous. In addition, the process may be a batch or continuous process.

5

Advantageously, one by-product in the production of MAA may be hydroxy isobutyric acid (HIB) which exists in equilibrium with the product MAA at the conditions used for decomposition of the dicarboxylic acids. Accordingly,
10 partial or total separation of the MAA from the products of the decomposition reaction shifts the equilibrium from HIB to MAA thus generating further MAA during the process or in subsequent processing of the solution after separation of MAA.

15

As mentioned above, the source of pre-acid such as citric acid, isocitric acid or aconitic acid preferably decomposes under suitable conditions of temperature and pressure and optionally in the presence of base catalyst to one of the
20 dicarboxylic acids of the invention. Suitable conditions for this decomposition are less than 350°C, typically, less than 330°C, more preferably, at up to 310°C, most preferably at up to 300°C. In any case, a preferred lower temperature for the decomposition is 100°C. Preferred
25 temperature ranges for the source of pre-acid decomposition are between 110 and up to 349°C, more preferably, between 120 and 300°C, most preferably, between 130 and 280°C, especially between 140 and 260°C.

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

To maintain the reactants in the liquid phase under the above source of pre-acid decomposition temperature conditions the decarboxylation reaction is carried out at
5 suitable pressures at or in excess of atmospheric pressure. Suitable pressures which will maintain the reactants in the liquid phase in the above temperature ranges are greater than 15psia, more suitably, greater than 20psia, most suitably, greater than 25psia and in any case at a higher
10 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
15 typically, at less than 4000 psia.

Preferably, the source of pre-acid decomposition reaction is at a pressure of between about 15 and 10000psia. More preferably, the reaction is at a pressure of between about
20 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
25 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.

30

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.

The chemicals used in these experiments were all obtained from Sigma Aldrich; Itaconic acid ($\geq 99\%$) (Catalogue number: I2,920-4); citraconic acid ($98+\%$) (Catalogue number C82604); mesaconic acid (99%) (Catalogue number: 13,104-0) and sodium hydroxide ($>98\%$) (Catalogue number S5881).

The procedure for these experiments is as follows.

The feed solution for the experiment was prepared by mixing together a di-carboxylic acid (either itaconic, citraconic or mesaconic acid) (65 g, 0.5 moles) and sodium hydroxide (20 g, 0.5 moles). The two solids were then dissolved in 915 g de-ionised water to give a total feed solution weight of 1 kg.

The reaction solution was then fed into the ThalesNano X-Cube Flash apparatus at the required flow rate to obtain 120, 240, 366, 480, 600 and 870 seconds residence times. Every experiment was carried out at a set pressure of 150

bar (2176 psi). The temperature of the reactor was adjusted according to the requirements of each experiment.

X-Cube Flash Operation

5

Ensure both pump lines are attached and immersed in solvent. Set the reaction pressure to the required pressure (150 bar). Set the reaction temperature to the required temperature. Ensure that the feed line for pump 1 is
10 inserted into the reactant feed solution bottle. Select pump 1 and set to the required flow rate of the feed solution to achieve the desired residence time of the solution in the reactor. Start the experiment and run the pump for 20 minutes. After running the pump for 20 minutes
15 start to collect the liquid sample exiting the X-cube.

After sufficient reactor exit has been collected, the X-Cube will need to be flushed with water to avoid cross contamination between experimental samples. Ensure that the feed line for pump 2 is inserted into the water feed
20 bottle. Switch the liquid feed to the reactor from that fed from pump 1 (reactant solution) to that fed from pump 2 (water). Run the pump for 20 minutes so that no reactant solution is left in the reactor.

25 Analysis

All reaction exit solutions were analysed by ^1H NMR spectroscopy. All samples were run on either a 500Mhz JOEL spectrometer or a 300Mhz JOEL spectrometer. All NMR spectra
30 that were observed were analysed and the relative mol% of the individual components calculated on the basis of the observed integrals.

A series of decarboxylation experiments were carried out on itaconic (IC), citraconic (CC) and mesaconic (MC) acid at
5 various temperatures and residence times according to the above procedure. The results are shown below.

Table 1 Conversion and Selectivity for the Decarboxylation of Citraconic acid at Various Temperatures and Residence Times

			relative mol%								mol%
Ex.	Residence time/secs	Temp°C	MC	IC	CC	PC	MAA	HIB	TBP	% Conv.	Sel.
1	870.00	150.00	1.69	22.33	71.11	3.28	1.59	0.00	0.00	1.59	100.00%
2	870.00	160.00	7.47	19.91	51.75	11.27	9.60	0.00	0.00	9.60	100.00%
3	870.00	170.00	11.05	15.70	41.58	14.14	15.48	1.77	0.29	17.25	98.17%
4	870.00	180.00	14.90	9.10	26.39	1.38	39.92	6.32	1.98	46.24	95.27%
5	600.00	170.00	1.12	21.33	74.40	1.82	1.29	0.04	0.00	1.33	100.00%
6	600.00	180.00	5.02	20.39	60.54	8.22	5.82	0.00	0.00	5.82	100.00%
7	600.00	190.00	10.80	17.09	42.25	8.94	19.35	1.29	0.27	20.64	98.62%
8	480.00	180.00	0.87	19.64	77.31	0.83	0.97	0.38	0.00	1.35	100.00%
9	480.00	190.00	1.58	19.22	69.80	4.99	4.08	0.33	0.00	4.41	100.00%
10	366.00	190.00	0.00	18.26	78.28	2.33	1.14	0.00	0.00	1.14	100.00%

5

Key: MC Mesaconic Acid
 IC Itaconic Acid
 CC Citraconic Acid
 10 PC Paraconic Acid
 MAA Methacrylic acid
 HIB Hydroxyisobutyric acid
 TBP Total By-Products
 Conv. Conversion
 15 Sel. Selectivity

Table 2 Conversion and Selectivity at Various Temperatures and Residence Times for Itaconic acid Decarboxylation

			relative mol%								Mol%
Ex .	Residence time/secs	Temp°C	MC	IC	CC	PC	MAA	HIB	TBP	% Conv.	Sel.
11	870.00	130.00	0.88	73.55	20.95	4.53	0.09	0.00	0.00	0.09	100.00%
12	870.00	140.00	6.28	32.40	47.21	11.49	2.62	0.00	0.00	2.62	100.00%
13	870.00	150.00	4.57	31.70	47.79	13.12	2.82	0.00	0.00	2.82	100.00%
14	870.00	160.00	7.99	26.53	45.50	12.82	7.16	0.00	0.00	7.16	100.00%
15	870.00	170.00	15.71	15.55	36.35	8.91	23.46	0.00	0.02	23.47	99.94%
16	870.00	180.00	16.23	15.16	36.48	4.06	27.26	0.00	0.81	27.26	97.11%
17	870.00	190.00	12.50	6.78	17.12	0.08	48.78	10.93	3.81	59.70	92.75%
18	600.00	140.00	1.35	74.40	21.43	1.82	1.01	0.00	0.00	1.01	100.00%
19	600.00	150.00	3.80	67.63	23.06	4.65	0.85	0.00	0.00	0.85	100.00%
20	600.00	160.00	5.18	34.74	43.07	15.17	1.84	0.00	0.00	1.84	100.00%
21	600.00	170.00	8.36	22.42	49.36	14.24	5.61	0.00	0.00	5.61	100.00%
22	600.00	180.00	10.30	19.46	44.39	12.64	13.21	0.00	0.00	13.21	100.00%
23	600.00	190.00	15.43	16.11	36.81	8.58	22.23	0.00	0.84	22.23	96.36%
24	480.00	150.00	1.42	84.81	9.92	3.67	0.18	0.00	0.00	0.18	100.00%
25	480.00	160.00	1.94	65.20	27.20	3.12	2.54	0.00	0.00	2.54	100.00%
26	480.00	170.00	3.61	41.70	40.95	11.21	2.54	0.00	0.00	2.54	100.00%
27	480.00	180.00	6.81	24.07	50.04	13.47	5.61	0.00	0.00	5.61	100.00%
28	480.00	190.00	11.39	20.21	45.84	10.71	11.85	0.00	0.00	11.85	100.00%
29	366.00	170.00	1.92	71.93	21.96	3.84	0.35	0.00	0.00	0.35	100.00%
30	366.00	180.00	3.86	48.12	37.28	9.36	1.38	0.00	0.00	1.38	100.00%
31	366.00	190.00	5.81	31.23	44.72	12.11	6.14	0.00	0.00	6.14	100.00%
32	240.00	180.00	0.90	84.15	14.03	0.37	0.55	0.00	0.00	0.55	100.00%
33	240.00	190.00	1.70	70.52	25.32	1.04	1.42	0.00	0.00	1.42	100.00%
34	120.00	180.00	1.01	87.52	7.88	3.30	0.29	0.00	0.00	0.29	100.00%
35	120.00	190.00	0.53	79.63	15.87	3.21	0.76	0.00	0.00	0.76	100.00%

Table 3 Conversion and Selectivity at Various Temperatures and Residence Times for Mesoconic acid Decarboxylation

			relative mol%								Mol%
Ex .	Residence time/secs	Temp° C	MC	IC	CC	PC	MAA	HIB	TBP	% Conv.	Sel.
36	870.00	150.00	86.43	6.69	6.54	0.00	0.34	0.00	0.00	0.34	100.00%
37	870.00	160.00	55.53	10.71	21.96	4.81	6.44	0.56	0.00	6.99	100.00%
38	870.00	170.00	33.29	12.00	32.26	15.95	5.42	0.81	0.28	6.23	95.06%
39	870.00	180.00	13.58	8.51	20.58	0.27	44.61	8.35	4.09	52.97	91.59%
40	870.00	190.00	10.51	5.46	14.70	1.09	51.67	12.62	3.95	64.29	92.89%
41	600.00	170.00	69.89	8.74	16.48	2.61	2.27	0.00	0.00	2.27	100.00%
42	600.00	180.00	47.32	13.07	26.38	1.80	11.43	0.00	0.00	11.43	100.00%
43	600.00	190.00	29.39	12.25	26.69	5.78	25.38	0.00	0.52	25.38	97.99%
44	480.00	180.00	69.19	9.29	15.66	2.66	3.20	0.00	0.00	3.20	100.00%
45	480.00	190.00	49.50	11.33	25.03	5.50	8.34	0.30	0.00	8.64	100.00%
46	366.00	180.00	86.44	6.56	5.87	0.00	1.13	0.00	0.00	1.13	100.00%
47	366.00	190.00	77.51	8.15	10.46	2.97	0.91	0.00	0.00	0.91	100.00%

As can be seen from tables 1-3, the selectivity of the decarboxylation at low temperatures to the desired methacrylic acid product is surprisingly high and as much as 100% in many cases.

5

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 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 at a temperature in the range from 100 to 199°C.
2. A process according to claim 1, wherein the dicarboxylic acid(s) reactant(s) or the source of pre-acids thereof are exposed to the reaction conditions for a time period of between about 75 seconds and 90000 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 100 and 199°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 reaction is at a temperature and pressure at which the reaction medium is in the liquid phase, typically, the reaction medium is an aqueous solution.

5. A process according to any preceding claim, wherein the temperature range for the process is between 110°C and up to 190°C.
- 5 6. A process according to any preceding claim, wherein the reaction is at a pressure range of between about 20 and 10000psia.
- 10 7. A process according to any preceding claim, wherein the catalyst comprises a source of OH⁻ions.
- 15 8. 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 compound of one of the above; or one or more amines; more preferably a Group I or Group II metal oxide, hydroxide, 20 carbonate, acetate, alkoxide, hydrogencarbonate or salt of a di- or tri-carboxylic acid or methacrylic acid.
- 25 9. A process according to any preceding claim, wherein the base catalyst is selected from one or more of the group consisting of LiOH, NaOH, KOH, Mg(OH)₂, Ca(OH)₂, Ba(OH)₂, CsOH, Sr(OH)₂, RbOH, NH₄OH, Li₂CO₃, Na₂CO₃, K₂CO₃, Rb₂CO₃, Cs₂CO₃, MgCO₃, CaCO₃, SrCO₃, 30 BaCO₃, (NH₄)₂CO₃, LiHCO₃, NaHCO₃, KHCO₃, RbHCO₃,

CsHCO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, $\text{Sr}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$,
 NH_4HCO_3 , Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , MgO , CaO , SrO ,
 BaO , $\text{Li}(\text{OR}^1)$, $\text{Na}(\text{OR}^1)$, $\text{K}(\text{OR}^1)$, $\text{Rb}(\text{OR}^1)$, $\text{Cs}(\text{OR}^1)$,
 $\text{Mg}(\text{OR}^1)_2$, $\text{Ca}(\text{OR}^1)_2$, $\text{Sr}(\text{OR}^1)_2$, $\text{Ba}(\text{OR}^1)_2$, $\text{NH}_4(\text{OR}^1)$ where
5 R^1 is any C_1 to C_6 branched, unbranched or cyclic
alkyl group, being optionally substituted with one
or more functional groups; $\text{NH}_4(\text{RCO}_2)$, $\text{Li}(\text{RCO}_2)$,
 $\text{Na}(\text{RCO}_2)$, $\text{K}(\text{RCO}_2)$, $\text{Rb}(\text{RCO}_2)$, $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$,
 $\text{Ca}(\text{RCO}_2)_2$, $\text{Sr}(\text{RCO}_2)_2$ or $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is
10 selected from, mesaconate, citraconate, itaconate,
citrate, oxalate and methacrylate; $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$,
 $\text{Li}_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$, $\text{K}_2(\text{CO}_2\text{RCO}_2)$, $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$,
 $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$, $\text{Mg}(\text{CO}_2\text{RCO}_2)_2$, $\text{Ca}(\text{CO}_2\text{RCO}_2)_2$, $\text{Sr}(\text{CO}_2\text{RCO}_2)_2$,
 $\text{Ba}(\text{CO}_2\text{RCO}_2)_2$, $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, where CO_2RCO_2 is selected
15 from mesaconate, citraconate, itaconate and oxalate;
 $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Li}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $\text{Sr}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
20 $\text{Ba}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, where
 $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is selected from citrate, isocitrate and
aconitate; methylamine, ethylamine, propylamine,
butylamine, pentylamine, hexylamine,
cyclohexylamine, aniline; and R_4NOH where R is
25 selected from methyl, ethyl propyl, butyl. More
preferably, the base is selected from one or more of
the following: LiOH , NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$,
 $\text{Ba}(\text{OH})_2$, CsOH , $\text{Sr}(\text{OH})_2$, RbOH , NH_4OH , Li_2CO_3 , Na_2CO_3 ,
 K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , MgCO_3 , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, LiHCO_3 ,
30 NaHCO_3 , KHCO_3 , RbHCO_3 , CsHCO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$,

$\text{Sr}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$, NH_4HCO_3 , Li_2O , Na_2O , K_2O , Rb_2O ,
 Cs_2O , ; $\text{NH}_4(\text{RCO}_2)$, $\text{Li}(\text{RCO}_2)$, $\text{Na}(\text{RCO}_2)$, $\text{K}(\text{RCO}_2)$,
 $\text{Rb}(\text{RCO}_2)$, $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$, $\text{Ca}(\text{RCO}_2)_2$, $\text{Sr}(\text{RCO}_2)_2$ or
 $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is selected from itaconate,
5 citrate, oxalate, methacrylate; $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$,
 $\text{Li}_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$, $\text{K}_2(\text{CO}_2\text{RCO}_2)$, $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$,
 $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$, $\text{Mg}(\text{CO}_2\text{RCO}_2)$, $\text{Ca}(\text{CO}_2\text{RCO}_2)$, $\text{Sr}(\text{CO}_2\text{RCO}_2)$,
 $\text{Ba}(\text{CO}_2\text{RCO}_2)$, $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, where CO_2RCO_2 is selected
from, mesaconate, citraconate, itaconate, oxalate;
10 $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Li}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $\text{Sr}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,
 $\text{Ba}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, where
15 $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is selected from citrate, isocitrate;
tetramethylammonium hydroxide and tetraethylammonium
hydroxide. Most preferably, the base is selected
from one or more of the following: NaOH , KOH ,
 $\text{Ca}(\text{OH})_2$, CsOH , RbOH , NH_4OH , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 ,
20 Cs_2CO_3 , MgCO_3 , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, $\text{NH}_4(\text{RCO}_2)$, $\text{Na}(\text{RCO}_2)$,
 $\text{K}(\text{RCO}_2)$, $\text{Rb}(\text{RCO}_2)$, $\text{Cs}(\text{RCO}_2)$, $\text{Mg}(\text{RCO}_2)_2$, $\text{Ca}(\text{RCO}_2)_2$,
 $\text{Sr}(\text{RCO}_2)_2$ or $\text{Ba}(\text{RCO}_2)_2$, where RCO_2 is selected from
itaconate, citrate, oxalate, methacrylate;
 $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, $\text{Na}_2(\text{CO}_2\text{RCO}_2)$, $\text{K}_2(\text{CO}_2\text{RCO}_2)$,
25 $\text{Rb}_2(\text{CO}_2\text{RCO}_2)$, $\text{Cs}_2(\text{CO}_2\text{RCO}_2)$, $\text{Mg}(\text{CO}_2\text{RCO}_2)$, $\text{Ca}(\text{CO}_2\text{RCO}_2)$,
 $(\text{NH}_4)_2(\text{CO}_2\text{RCO}_2)$, where CO_2RCO_2 is selected from
mesaconate, citraconate, itaconate, oxalate;
 $(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Na}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
 $\text{K}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Rb}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, $\text{Cs}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$,
30 $\text{Mg}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$, $\text{Ca}_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)_2$,

$(\text{NH}_4)_3(\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2)$, where $\text{CO}_2\text{R}(\text{CO}_2)\text{CO}_2$ is selected from citrate, isocitrate; and tetramethylammonium hydroxide.

- 5 10. A process according to any preceding claim, wherein the effective mole ratio of base OH^- :acid is between 0.001-2:1.
- 10 11. A process according to any preceding claim, wherein the concentration of the dicarboxylic acid reactant(s) is in the range 0.05M-20M.
- 15 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 at least 0.1M or greater, preferably in an aqueous source thereof.
- 20 13. 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.
- 25 14. A process according to any preceding claim, wherein the reaction pH is between about 2 and 9.
- 30 15. A process for the production of methacrylic acid comprising:- providing a source of a pre-acid selected from aconitic, citric and/or isocitric acid; performing a decarboxylation and, if

5 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 any one of claims 1 - 14.

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

15 17. A process according to claims 15 or 16, wherein the source of pre-acid decomposition reaction is at a pressure of between about 15 and 10000psia.

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

20 (i) preparation of methacrylic acid in accordance with the process of claims 1 - 17;

(ii) optional esterification of the methacrylic acid prepared in (i) to produce the methacrylic acid ester;

25 (iii) polymerisation of the methacrylic acid prepared in (i) and/or the ester prepared in (ii), optionally with one or more comonomers, to produce polymers or copolymers thereof.

19. A method according to claim 18, wherein the methacrylic acid ester of (ii) above is selected from C₁-C₁₂ alkyl or C₂-C₁₂ hydroxyalkyl, glycidyl, isobornyl, dimethylaminoethyl, tripropyleneglycol esters, more preferably, ethyl, n-butyl, i-butyl, hydroxymethyl, hydroxypropyl or methyl methacrylate, most preferably, methyl methacrylate, ethyl acrylate, butyl methacrylate or butyl acrylate.
20. A method according to claims 18 or 19, wherein the comonomers are selected from the group consisting of monoethylenically unsaturated carboxylic acids, and dicarboxylic acids and their derivatives, such as esters, amides and anhydrides.
21. A method according to claim 20, wherein the comonomers are selected from the group consisting of acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, iso-bornyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, lauryl methacrylate, glycidyl methacrylate, hydroxypropyl methacrylate, iso-bornyl methacrylate, dimethylaminoethyl methacrylate, tripropyleneglycol diacrylate, styrene, α -methyl styrene, vinyl acetate,

isocyanates including toluene diisocyanate and p,p'-methylene diphenyl diisocyanate, acrylonitrile, butadiene, butadiene and styrene (MBS) and ABS subject to any of the above comonomers not being the
5 momomer selected from methacrylic acid or a methacrylic acid ester in (i) or (ii) above in any given copolymerisation of the said acid monomer in (i) or a said ester monomer in (ii) with one or more of the comonomers.

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22. Polymethacrylic acid, polymethylmethacrylate (PMMA) and polybutylmethacrylate homopolymers or copolymers formed from the method of any one of claims 18 - 21.

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

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24 A method of preparing polymer or copolymers as described herein.