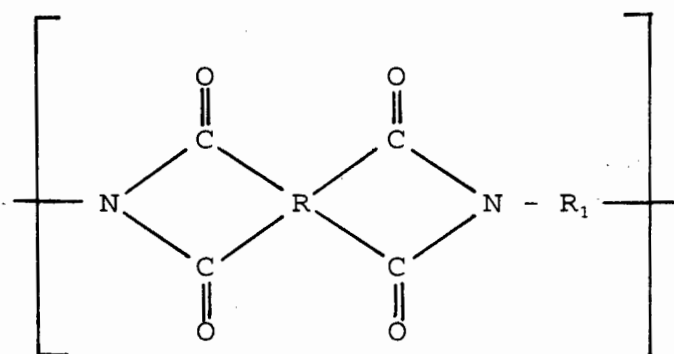


Thermoset Cross-Linked Polyimides

The present invention relates to thermoset cross-linked polyimides, in particular to a novel process for their preparation from polyamide acid precursors, polyimide articles obtainable thereby and novel polyamide acid precursors.

Polyimides are of particular use in the manufacture of articles such as films and sheets.

Of particular interest are thermoset cross-linked polyimides in which two imide groups are linked with one or more benzene rings. Such polyimides contain, for example, the following recurring structural units



wherein R is a tetravalent aromatic radical with at least one benzenoid ring and R₁ is a divalent organic radical comprising at least one benzene ring.

These polyimides may be manufactured by reacting dianhydrides with diamines and converting the polyamide acids thus obtained into polyimides with the elimination of water and cyclisation.

Document I describes a process for preparing polyimides in which approximately equimolar amounts of pyromellitic acid dianhydride and a diamine of the following structural formula: H₂N-R-NH₂, wherein R is a divalent group of an aromatic radical, are reacted in an organic solvent. A solution of one of the reaction components is added slowly to a solution of the other reaction component. With solid reaction components a dry mixture of the two components may first be prepared and this added slowly to the solvent.

The reaction mixture is kept at a temperature below 60°C, producing a viscous solution containing at least 50% polyamide acid which is then heated to between 350 and 550°C, so that the polyamide acid is converted to the polyimide.

Articles made from these polyimides possess excellent physical and chemical properties: they display high strength and heat-resistance and are also highly resistant to attack by a large number of chemicals.

Owing to the considerable strength of polyimides it is, however, difficult to produce shaped articles from them. The tendency is therefore to produce such structures from the intermediate, that is to say polyamide acids, and only subsequently to convert these into polyimides by heating to the required temperature.

Document II describes a process for preparing polyimides by reacting pyromellitic acid dianhydride with an aromatic diamine, the reaction being carried out in two stages. In a first stage, a condensation reaction in the presence of an organic solvent produces a soluble pyromellitic amide acid which, in a second stage, is converted by heating and with the elimination of water into a thermally stable polypyromellitic imide. Heating to 400°C is necessary to achieve total conversion.

Document II overcomes the problem of moulding articles by applying heat to articles compacted from the polyamide acid precursors.

In the process of Document II, a polyamide acid powder containing up to 80% by weight is compacted by pressure of 15 to 60 N/mm², and the compacted material is then sintered at a temperature of 250 to 400°C and under a pressure of 14 to 21 N/cm². Pressure and temperature values must be carefully selected so as to enable the water to escape from the compacted material.

The process of Document II is not however suitable for the manufacture of polyimide films or sheets.

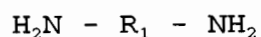
In the known processes for converting polyamide acid precursors to polyimides, the temperature has to be carefully regulated to prevent water produced as water vapour during the conversion of the polyamide into polyimide from being trapped in the compound as it sets. Otherwise, this may result in the formation of voids, which severely reduces the strength of the polyimides. Despite efforts to regulate temperature, it has often been impossible to prevent the occurrence of voids.

The problem which the present invention sets out to solve is therefore the provision of a process for the manufacture of polyimide articles which ensures that voids are not formed by trapping of water vapour.

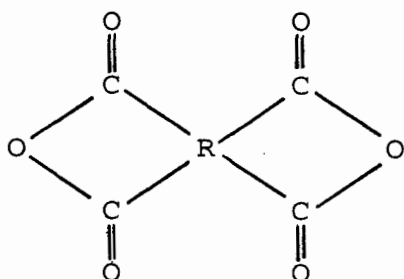
This problem is solved by the chemical process of the present invention.

We have now developed a process according to which the dehydration and cyclisation of the polyamide acid is brought about using a chemical route. The polyimide is thus formed at a much lower temperature than that temperature needed for the purely thermal heat-treatment method previously used.

The process of the present invention uses a polyamide acid prepared from a diamine of the structural formula:



wherein R_1 is a divalent radical containing at least one aromatic ring, which is reacted with at least one dianhydride of an aromatic tetracarboxylic acid having the following structural formula



wherein R is a tetravalent radical containing at least one aromatic ring and the four carbonyl groups are attached to different aromatic carbon atoms of R.

The reaction is carried out in a polar organic solvent at a temperature below 120°C . As a minimum temperature 20°C should be maintained. A polyamide acid is formed as intermediate product. This is subsequently converted into polyimide by treatment with an anhydride of a lower aliphatic monocarboxylic acid such as acetic acid anhydride.

According to the present invention there is provide [CLAIM 1]

The formation of the polyimide could be shown by infrared spectroscopy. With progressive conversion of the polyamide acid a clear shift in the absorption band from 3.1 to $13.85\ \mu\text{m}$ is observed.

In the process of the invention shaped articles are formed from the polyamide acid intermediate prior to conversion to the polyimide, which polyimide is difficult to shape.

Moulding may take place as soon as the reaction mixture has been partly converted into polyamide acid, for example as soon as a conversion of the reaction mixture of 50% has been achieved.

Accordingly the invention provides [CLAIM 15]

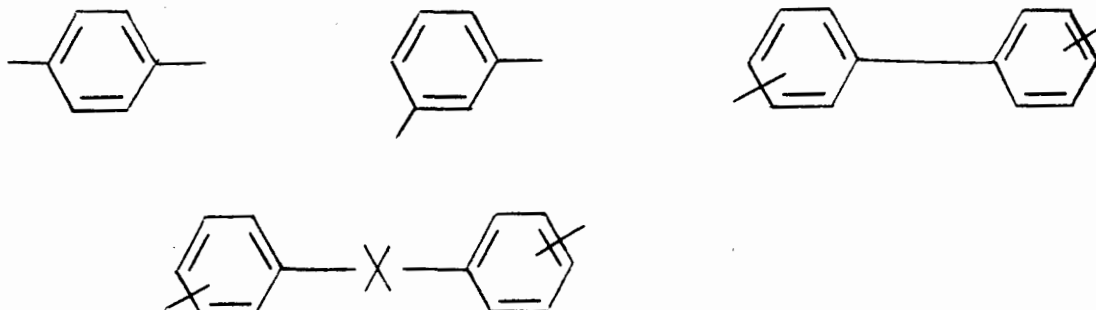
Solutions with a small polyamide acid content (less than 15% by weight) - which are not suitable for the manufacture of shaped articles - can be used as coating compositions. They may be used to coat metal objects such as sheets or wires, and woven plastics. Subsequent treatment with the aliphatic carboxylic acid anhydride produces a polyimide film.

In a further aspect the invention provides [CLAIM 14]

To produce the polyamide acid, approximately equimolar amounts of the said diamine and the dianhydride are mixed as dry solids. The mixture obtained is then added, in small proportions and with stirring, to the organic solvent. This method provides good control of the chemical process, which involves an exothermic reaction. The reaction mixture must be stirred until no further increase in the

viscosity of the solution is detectable. The polyamide acid content of the solution is then approximately 40%.

The aromatic radical designated R_1 in the structural formula for the diamine may consist of one of the following groups



wherein X is an alkylene group with 1 to 3 carbon atoms, sulphur, SO_2 or oxygen.

Among the diamines which are particularly suitable are those with two rings, for example:

benzidine
 4,4'-diamino-diphenyl methane
 4,4'-diamino-diphenyl propane
 4,4'-diamino-diphenyl ether
 4,4'-diamino-diphenyl sulphide
 4,4'-diamino-diphenyl sulphone.

When the latter two diamines are used, the compounds produced display particularly good properties, in particular the films made from them have excellent tensile strength.

The invention therefore provides [CLAIM 5]

Examples of aromatic tetracarboxylic acid dianhydrides of the above formula are in particular:

pyromellitic acid dianhydride (1, 2, 4, 5-benzene tetracarboxylic acid dianhydride)
 2,3,6,7-naphthalene tetracarboxylic acid dianhydride
 3,3',4,4'-diphenyl tetracarboxylic acid dianhydride
 3,4,3',4'-benzophenone tetracarboxylic acid dianhydride.
 [CLAIM 6]

The polar solvent used in the polymerisation process must dissolve, but not react with, at least one of the reactants. The solvent selected should preferably also act as a solvent for the polyamide acid intermediate formed.

Solvents that meet these requirements particularly well are

N,N-dimethylformamide and
 N,N-dimethylacetamide.

These two solvents may easily be removed by evaporation from the reaction products formed. The invention provides a process [CLAIM 8]

Apart from acetic acid anhydride, mentioned above, one can also use as dehydrating and cyclising agents for the polyamide acid formed from the reaction, propionic acid anhydride, butyric acid anhydride and isobutyric acid anhydride and mixtures thereof. The use of these anhydrides forms part of the present invention [CLAIM 3]

It is advantageous to add a diluent to the anhydride. In this way a better diffusion of the anhydride through the polyamide acid structure is achieved. Mostly benzene is used as diluent but cyclohexane, carbon tetrachloride or acetonitrile may also be used. [CLAIMS 9 + 10]

It is also highly desirable to add to the anhydride of the lower aliphatic carboxylic acid a tertiary amine such as pyridine, 4-benzylpyridine, 3,4-lutidine or isoquinoline. The tertiary amine acts as a catalyst for the conversion of the polyamide acid into polyimide. It largely prevents the polymer from being degraded by hydrolysis and promotes ring closure. The tertiary amine, such as pyridine, may be used in such a quantity that its molar proportion to the anhydride is 1:1. [CLAIM 11]

Among the particularly effective amines are trimethylamine and triethylamine. These accelerate the conversion of the polyamide acid to the polyimide even more effectively than pyridine. Smaller quantities than used for pyridine are exceptionally effective. [CLAIM 12]

Shaped polyimide articles which can advantageously be produced by our process are, in particular, self-supporting films or sheets. By extrusion of the viscous polyamide acid solution films can be produced that are subsequently passed through an acid anhydride bath where conversion to polyimide by cyclisation occurs. The polyimide films are flexible and tear-resistant.

According to another procedure, a solution of polyamide acid is cast on a support having a smooth surface, for example a glass plate, and the viscous solution is spread over the support with a doctor blade to form a thick film. The coated support is then, for example, immersed in an acetic acid anhydride bath where dehydration and cyclisation of the polyamide acid to the polyimide occurs.

The invention provides [CLAIM 16]

It was found that the film removed from the support showed an asymmetric structure with a thin, slightly-porous skin and a thicker, porous layer. The skin was the top layer which had been directly exposed to the cyclising solution, while the porous layer was the side face-down on the support. Accordingly asymmetrically structured polyimide articles form part of the present invention.

The microporous sheet produced had selective permeability properties. It proved to be highly suitable for use as a semipermeable membrane for the separation of mixtures of liquids and gases in reverse osmosis or ultrafiltration.

In a further aspect the invention provides [CLAIM 17]

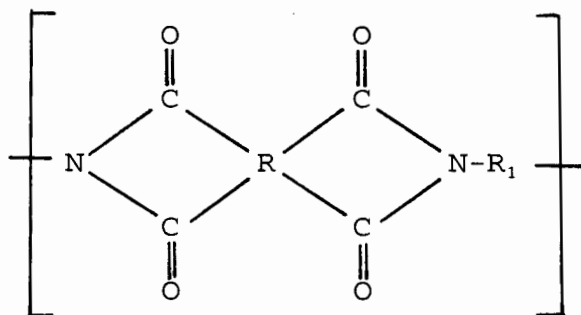
The membrane should be between 100 and 300 μm thick, since a thinner membrane has insufficient strength in many instances while a thicker membrane is often insufficiently permeable to the solvent. [CLAIM 18]

The invention also provides [CLAIM 19]

A number of examples illustrating the process of the invention follows.

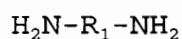
Claims (all Contracting States except Spain)

1. A process for preparing a thermoset cross-linked polyimide containing the recurring structural unit:

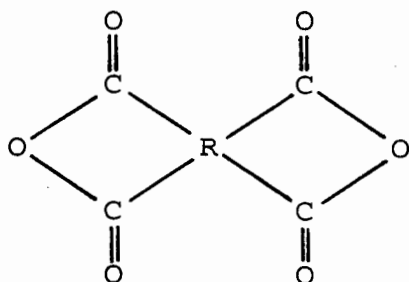


wherein R is a tetravalent aromatic radical with at least one benzenoid ring and R_1 is a divalent organic radical comprising at least one benzene ring, which process comprises dehydration and cyclisation of the corresponding polyamide acid precursor, characterised in that the dehydration and cyclisation is brought about by a chemical reaction comprising treatment of the polyamide acid precursor with an anhydride of a lower aliphatic monocarboxylic acid.

2. A process as claimed in claim 1 wherein the polyamide acid precursor is formed by reaction of a diamine of structural formula:

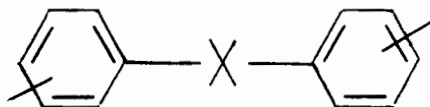


wherein R_1 is as defined in claim 1, with at least one dianhydride of an aromatic tetracarboxylic acid of structural formula:



wherein R is as defined in claim 1 and the four carbonyl groups are attached to different aromatic carbon atoms of the group R, the reaction being carried out in a polar organic solvent in the temperature range 20 to 120°C.

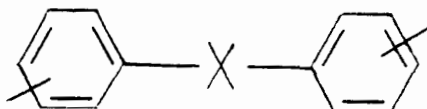
3. A process as claimed in claim 1 or 2 wherein the anhydride of the lower aliphatic monocarboxylic acid is acetic acid anhydride, propionic acid anhydride, butyric acid anhydride, isobutyric acid anhydride or mixtures thereof.
4. A process as claimed in any one of claims 1 to 3 wherein the aromatic radical R_1 has the formula:



wherein X is an alkylene group with 1 to 3 carbon atoms, sulphur, SO_2 , oxygen or a bond.

5. A process as claimed in claim 4 wherein R_1 is 4,4'-diamino-diphenyl sulphide or 4,4'-diamino-diphenyl sulphone.
6. A process as claimed in any one of claims 1 to 5 wherein the aromatic tetracarboxylic acid dianhydride is pyromelletic acid dianhydride, 2,3,6,7-naphthalene tetracarboxylic acid dianhydride, 3,3',4,4'-diphenyl tetracarboxylic acid dianhydride or 3,4,3',4'-benzophenone tetracarboxylic acid dianhydride.
7. A process as claimed in any one of claims 1 to 6 wherein the chemical dehydration and cyclisation is carried out in the presence of an inert polar solvent.
8. A process as claimed in claim 7 wherein the inert polar solvent is N,N-dimethylformamide or N,N-dimethylacetamide.
9. A process as claimed in claim 7 or 8 further comprising a diluent.
10. A process as claimed in claim 9 wherein the diluent is benzene, cyclohexane, carbon tetrachloride or acetonitrile.

11. A process as claimed in any one of claims 7 to 10 further comprising a tertiary amine catalyst.
12. A process as claimed in claim 11 wherein the tertiary amine catalyst is trimethylamine or triethylamine.
13. A polyamide acid precursor obtainable by the process described in claim 2 when R_1 has the formula:



and X is sulphur or SO_2 .

14. A method of coating an article with a polyimide film comprising:
- (i) coating the article with a solution of a polyamide acid precursor prepared as described in claim 2, wherein the polyamide acid content is less than 15% by weight; and
 - (ii) treating the coated article with an aliphatic carboxylic acid anhydride.
15. A method of preparing shaped polyimide articles comprising extrusion of a viscous polyamide acid solution wherein the polyamide acid content is at least 50% by weight, prepared as described in claim 2, and subsequently passing the extrusion through a bath containing an aliphatic carboxylic acid anhydride.
16. A method of preparing polyimide articles having an asymmetric structure comprising:
- (i) casting a viscous solution of a polyamide acid as prepared in claim 2 on a support having a smooth surface;
 - (ii) spreading the viscous solution over the support; and
 - (iii) immersing the casting in a bath containing an aliphatic carboxylic acid anhydride.
17. Polyamide articles obtainable by the method of claim 16.
18. Polyamide articles as claimed in claim 17 having a thickness between 100 and 300 μm .
19. Use of a polyamide article as claimed in claim 18 as a semipermeable membrane.

Notes to the Examiner

1. Reservations under Art. 167(2) EPC. Spain does not permit claims to chemical products per se. A separate claims set for Spain omitting product claims should therefore be prepared.

Separate claims for Greece are not required. There are no claims specifically directed to pharmaceutical products.

2. Claim 13 is directed to novel polyamide precursors per se. These are novel in view of the diamines (not described in the prior art) and are moreover inventive in view of the advantageous properties they confer on the polyimide products.
3. Although other polyamide precursors with two aromatic rings are novel, they are not claimed per se since it is not stated that they have distinguishing advantageous properties.
4. A claim to all polyimide products 'obtainable by' the process of claim 1 was considered. However, it is not certain that the materials are novel. The client's letter states only that in prior products it has "often" been impossible to prevent voids.
5. The 'porous' articles prepared by casting are however believed to be novel and have been claimed per se.