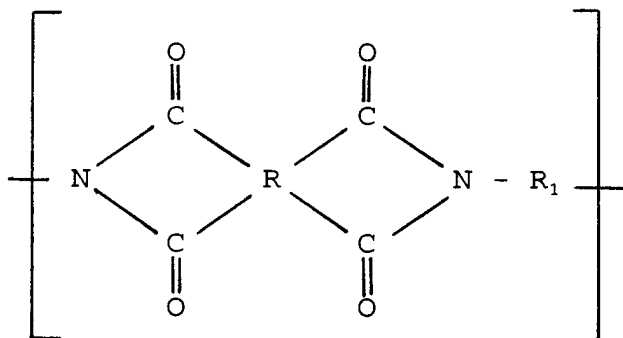


Candidate's examination paper (Examination paper B/1991 Chem

Revised Description of the Application

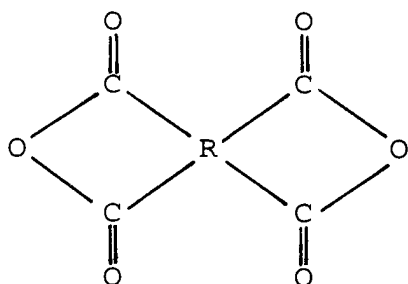
Process for the preparation of Polyimides and shaped articles produced therefrom

The invention relates to a process for preparing thermoset cross-linked polyimides in which two imide groups are linked with one or more benzene rings and which have 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.

Polyimides of this class are manufactured by a process as, for example, described in Document I; this involves reacting a diamine of the structural formula H₂N - R₁ - NH₂, wherein R₁ is a divalent radical containing at least one aromatic ring, in a polar organic solvent 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 polyamide acid intermediate product obtained is converted into polyimide by heating to between 350°C and 550°C with the elimination of water and cyclisation of the polyamide acid.

The articles made from these polyimides possess excellent physical and chemical properties: they display a high level of 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. As known from Document I, the tendency is now therefore to produce such structures from the polyamide acid intermediate which is subsequently converted to polyimide by heating to the required temperature.

One disadvantage of this known method is the fact that the temperature has to be carefully regulated to prevent water produced as water vapour during 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 is solved according to Document III by converting the polyamide acid obtained as an intermediate product into polyimide by treatment with an anhydride of a lower aliphatic monocarboxylic acid such as acetic acid anhydride.

Document III describes suitable amine precursors and aromatic tetracarboxylic acid dianhydrides for the preparation of polyamide acid intermediates such as to confer a modulus of elasticity of 2500 MPa, elongation of 7% and tensile strength of 100 MPa. Document III further describes suitable non-polar solvents and diluents for use in the polyimide process.

Document IV also describes the preparation of polyimides but by non-chemical conversion of polyamide acids. Document IV describes the use of tertiary amine catalysts to enhance the conversion process.

The present invention provides polyimide products conferring improved physical properties over those known in the art. In particular the invention provides a process for preparing polyimides with improved elasticity, elongation and tensile strength. In a further aspect, the invention provides polyimides having an asymmetric structure as hereinafter described, which confers further advantageous physical properties.

The formation of polyimide can 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 μm 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.

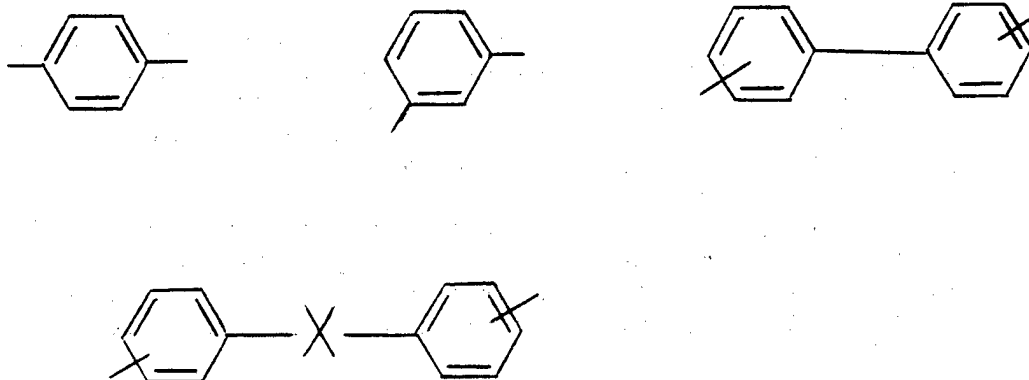
Moulding may take place as soon as the reaction mixture has been partly converted into polyamide acid, for example as soon as a conversion of the reaction mixture of 50% has been achieved.

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%.

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.

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.

Accordingly the invention provides [CLAIM 1]

Polyimide products prepared according to the above process using sulphur containing intermediates, and the polyamide acid precursors thereto also form part of the invention.

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.

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.

Apart from acetic acid anhydride, mentioned above, one can also use as dehydrating and cyclising agents for the polyamide acid formed from the reaction, other C₁₋₄ alkyl monocarboxylic acid anhydrides such as propionic acid anhydride, butyric acid anhydride and isobutyric acid anhydride and mixtures thereof.

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.

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 the 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.

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.

Shaped polyimide articles which can advantageously be produced according to the invention 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 more flexible and tear-resistant than those known in the art.

According to a preferred procedure of the invention 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.

Accordingly, the invention provides claim 4.

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.

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

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.

The following examples 5, 6 and 7 illustrate the processes of the invention. Examples 1 to 4 are included for the purposes of comparison only, so as to illustrate the advantageous physical properties of the polyimide products obtainable by the processes of the invention.

Example 1

14g of benzidine and 14g of pyromellitic acid dianhydride were mixed in the dry state and dissolved portionwise in 70 ml of dimethylacetamide with continuous stirring. Another 20 ml of dimethylacetamide was added, and after the diamine had reacted with the acid anhydride a polyamide acid solution with a polymer content of 22% by weight was obtained. The viscous solution of polyamide acid was moulded by extrusion into a self-supporting film which was immersed for 10 hours in a solution of 180 ml benzene, 80 ml acetic acid anhydride and 40 ml pyridine. The film was then vacuum-dried with heating at a temperature of 110°C. Infrared spectral analysis indicated that the film was of a polyimide. It was flexible but tear-resistant.

Example 2

The procedure was essentially the same as for Example 1 but no pyridine was added to the acetic acid anhydride solution. In this instance, conversion of the polyamide acid to polyimide took 15 hours.

Example 3

4,4'-Diamino-diphenyl propane, 12g, and pyromellitic acid dianhydride, 17g, were mixed to form a powdered mixture which was then added to 75 ml of dimethylformamide with continuous stirring with cooling. Another 30 ml of dimethylformamide was added so that a polyamide acid solution with a polymer component of 24.5% by weight resulted. Films produced from the solution were immersed in a solution consisting of 200 ml of benzene and 50 ml of acetic acid anhydride and to which 30 ml of pyridine had also been added. After an immersion time of 11 hours, the conversion of the polyamide acid to the polyimide was complete.

Example 4

A film produced from a polyamide acid solution in a similar manner to Example 3 was immersed in a solution containing 200 ml benzene and 50 ml acetic acid anhydride to which solution 18 ml of triethylamine had been added as tertiary amine. After an immersion time of 6 hours, that is, after a much shorter period than in Example 3, the conversion of the polyamide acid to the polyimide was complete.

Example 5

A mixture of 4,4'-diamino-diphenyl sulphone, 12g, and pyromellitic acid dianhydride, 10g, was added portionwise with continuous stirring and with cooling to 30 ml of dimethylformamide. Another 20 ml of dimethylformamide was then added. Reaction of the constituents produced a polyamide acid solution with a polymer content of 22% by weight. As in the previous examples, this was used to produce a self-supporting film which was immersed in a bath consisting of 15 parts cyclohexane, 1 part pyridine and 1 part acetic acid anhydride for 10 hours and then vacuum-dried at 120°C. The film proved to be highly tear-resistant.

Example 6

4,4'-diamino-diphenyl ether, 16g, and pyromellitic acid dianhydride, 18g, were reacted in dimethylacetamide as solvent to form a solution of polyamide acid (20% by weight). More dimethylacetamide was used to dilute the solution to a solids content of 10%, and the solution was then spread on a glass plate with a doctor blade to produce a 0.5 mm thick film. The glass plate supporting the film was immersed in a benzene solution containing 1 mole/l of pyridine and 1 mole/l of acetic acid anhydride. After being immersed for 10 hours in the solution, which was heated to 70°C, the film had become cloudy. Having been cyclised to polyimide the film was then removed from the glass plate, washed with benzene and dried at 80°C. The film produced was 0.3 mm thick and of asymmetric structure with a shiny, slightly porous skin on top and, underneath, a matt, fairly porous, thicker layer which had been face-down on the glass plate during cyclisation.

Example 7

Another sheet was produced in a similar manner to Example 6, the difference being that 4,4'-diamino-diphenyl sulphide, 16g, was used as the diamine. Again, a sheet with an asymmetric structure was obtained, but it showed a better tear-resistance than the membrane obtained in the previous example, presumably due to the diamine used.

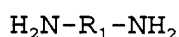
The sheets of asymmetric structure obtained in Examples 6 and 7 showed selective permeability properties to gases and liquids and proved to be highly suitable for use as microporous membranes.

The following table gives a summary of the properties of the films produced in Examples 1 to 7.

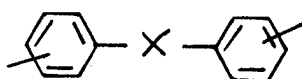
Example	Modulus of elasticity in MPa	Tensile strength in MPa	Elongation in %
1	2400	98	7
2	2480	102	9
3	2270	94	6
4	2300	100	8
5	3800	142	15
6	2670	112	8
7	3680	138	14

Revised Claims (all Contracting States excluding Spain)

1. A process for preparing polyimides in which a diamine of the structural formula:

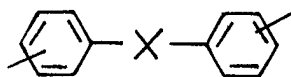


wherein R_1 is a divalent radical containing at least one aromatic ring is reacted with a dianhydride of an aromatic tetracarboxylic acid in an organic polar solvent at a temperature of between 20°C and 120°C until a polyamide acid intermediate product has formed which is then converted to polyimide by treatment of the polyamide acid with an anhydride of a C_{1-4} alkyl monocarboxylic acid, characterised in that R_1 in the diamine of formula $\text{H}_2\text{N}-\text{R}_1-\text{NH}_2$ is



where X is sulphur or SO_2 .

2. Polyimides obtainable by the process of claim 1.
3. A polyamide acid intermediate obtainable by the process of claim 1 wherein R_1 in the diamine of formula $\text{H}_2\text{N}-\text{R}_1-\text{NH}_2$ is



where X is sulphur or SO_2 .

4. A process for preparing cast polyimide articles in which
- (i) a viscous solution of a polyamide acid intermediate is formed from a diamine of the structural formula $\text{H}_2\text{N}-\text{R}_1-\text{NH}_2$ wherein R_1 is a divalent radical containing at least one aromatic ring, and a dianhydride of an aromatic

tetracarboxylic acid in an organic polar solvent temperature of between 20°C and 120°C;

- (ii) the intermediate is cast on a support having a smooth surface in the form of a thick film; and then
 - (iii) converted to polyimide by treatment with an anhydride of a C₁₋₄ alkyl monocarboxylic acid, characterised in that the conversion is carried out by immersing the coated support in a bath containing the anhydride of a C₁₋₄ alkyl monocarboxylic acid.
5. A process as claimed in claim 1 or 4 in which the treatment with the C₁₋₄ alkyl monocarboxylic acid anhydride takes place in the presence of a diluent.
 6. A process as claimed in any one of claims 1, 4 or 5 in which the treatment with C₁₋₄ alkyl monocarboxylic acid anhydride takes place in the presence of a tertiary amine catalyst.
 7. A process as claimed in claim 6 in which the molar ratio of the catalyst to the anhydride is 1:1.
 8. A process as claimed in any one of claims 4 to 7 in which the immersion bath is heated during the conversion process.
 9. A polyimide article obtainable by the process of any one of claims 4 to 8.
 10. A polyimide article as claimed in claim 9 in the form of a membrane, having a thickness between 100 and 300 µm.
 11. Use of a polyimide article as claimed in claim 10 as a semipermeable membrane.

18th April 1991

European Patent Office
Erhardtstrasse 27
D-8000 Munich
Germany

Dear Sirs,

Re: European Patent Application No.

This letter is in response to the Communication from the European Patent Office under Article 96(2) and Rule 51(2) EPC, dated

The Applicants acknowledge prior art Documents III and IV newly brought to their attention. Accordingly a revised claims set and

description (in triplicate) are submitted for further consideration by the Examiner.

The Applicants believe the newly-submitted claims to satisfy the requirements of the Convention. The following paragraphs are offered in support of the patentability of the revised claims. They address the observations numbered 1 to 6 of the Examiner's Communication and discuss the novelty and inventive step of the revised claims, pointing out, as appropriate, their basis in the application documents as filed.

Prior art Document III utilises a chemical process for conversion of polyamide acid intermediates to polyimides. This process overcomes the problems of voids forming in the polyimide due to trapping of water vapour when conversion is effected by heating.

Document III describes the preparation of polyimide films with a modulus of elasticity of 2500 MPa, elongation of 7% and strength of 100 MPa.

Document IV similarly concerns the preparation of polyimides and describes the use of tertiary amine catalysts to enhance the conversion from the polyamide acid intermediates.

Document IV does not however utilise a chemical conversion process. The process described is moreover unsuitable for the preparation of film products.

The problem which the present invention set out to solve, when viewed in the context of Document III (considered by the Applicants to represent the closest state of the art) is the preparation of polyimide products having improved physical properties.

This is achieved by using specific diamine starting materials which confer particular benefit with regard to elasticity, tensile strength and elongation.

Further physical features of benefit are derived from the novel casting process described at page 7 of the description, wherein the chemical conversion of the polyamide acid intermediates takes place using a film of polyamide acid on a solid support.

The independent claims will now be considered in more detail.

New claim 1 describes a process wherein the diamine starting material of formula $\text{NH}_2\text{-R}_1\text{-NH}_2$ has two phenyl groups separated by sulphur or a sulphone group.

It is submitted that these amines are novel in the context of the process for preparing polyimides. Their use is not described in any of the prior art documents. It is moreover submitted that their use in the process confers advantageous physical features which are surprising in relation to the prior art, thus conferring an inventive step. See table on page 10 of the description.

It is therefore respectfully submitted that new claim 1 is patentable within the meaning of Article 52 EPC.

Claim 2 is directed to the polyimide products obtainable by the process of claim 1. It is submitted that these products are novel per se in view of the diamine starting materials. As indicated above, these materials have surprising physical qualities.

New claim 3 is directed to the novel polyamide acid intermediates used in the process of claim 1. Board of Appeal Case Law has acknowledged the patentability of novel intermediate products when used in the preparation of patentable end products.

The Applicants respectfully submit that claim 3 is therefore patentable.

As referred to above, the particular 'casting' process described on page 7 of the description confers physical properties on polyimide films, not previously known.

The advantage of immersing a film of polyamide acid, cast on a solid support having a smooth surface, is that it produces a product with an asymmetric structure.

The Examiner will note from the description that the products have a porous structure which renders them particularly useful for use as semi-permeable membranes.

Document III describes a casting method for preparing polyimide films. It does not however, carry out the conversion process with the 'film' attached to the solid support. The Examiner will appreciate from the description at page 7 of the present specification that the asymmetric structure is achievable only when the conversion takes place on the support. Otherwise, a "double-skinned" product would be obtained which would not have the desired properties.

It is therefore submitted that new claim 4 is novel in the light of the prior art. Inventive step is, as described above, to be recognised in view of the unforeseen advantageous physical properties.

Dependent claims 4 to 8 further define preferred features of the conversion process.

New claims 9 and 10 are directed to novel polyamide articles obtainable by the above-described process.

It should be noted that claim 4 and claims 9 and 10 are not limited to products obtainable using the sulphur containing diamine precursors. The process of claim 4 is applicable using the whole range of starting materials and hence all polyamide acid intermediates.

Finally new claim 11 is directed to the novel use of polyimide articles, made by the process of claim 4, as semi-permeable membranes.

The Examiner will note that only films having the optimum thickness defined in claim 10 are considered to have utility for this purpose.

In relation to item 7 of the Examiner's Communication, the Applicants submit a revised description. The amendments acknowledge Documents III and IV as prior art and incorporate a reformulation of the problem which the invention sets out to solve in the light thereof.

The Examiner will note that the objection (item 6) under Article 84 has been attended to in both the description and the claims. Basis for C₁₋₄ alkyl is derived from the listed materials described at the top of page 6 of the description.

The Applicants trust that the Examining Division will now find the application in order for grant. If the Examiner has any outstanding queries or objections, he is cordially invited to contact the undersigned for further clarification.

In the event that a formal rejection is intended, oral proceedings under Article 116 EPC are requested.

Yours faithfully,

A. Representative
REPRESENTATIVE A.
Authorised representative for the Applicants

Notes to the Examiner

1. The revised claims relate to Contracting States other than Spain. In view of the reservation under Art. 167 EPC in relation to chemical products, a revised claims set, excluding product claims should accompany the response.
2. It is accepted that a divisional application may be required in view of unity objections under Art. 82 EPC.

The new process for the preparation of permeable products has not however been considered by the Examiner to date. The Applicants therefore retain the option, if a unity objection arises of maintaining either claim 1 or claim 4 in the present application.