EUROPEAN QUALIFYING EXAMINATION 1991

PAPER B
CHEMISTRY

This paper comprises:

INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent app for all the Contracting States comprising the appended docume has been filed and that the European Patent Office has communica the annexed official letter.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is now to draft a full response to the official letter. The official letter may or may not necessitate amendment of the description or claims or both and may or may not require arguments, for example as to the relevance of the prior art. You should bear in mind, in drafting your response, that the claims should afford the broadest possible protection. The response should be a letter to the EPO, but no particular form is mandatory. Any amendments should be clearly stated as insertions or deletions in the response or set out in a separate document. In any case, the amendments proposed should be sufficient to meet the requirements of the Convention as to both claims and description.

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* These documents do not necessarily constitute the only or best solution to the task set in Paper A (Chemistry).

If your response includes a proposal to make any part of the application the subject of a divisional application, you should suggest a text for at least the main claim of the divisional application and also indicate, where appropriate, your grounds for considering such claim to be acceptable. You need not however propose an introduction for any divisional application.

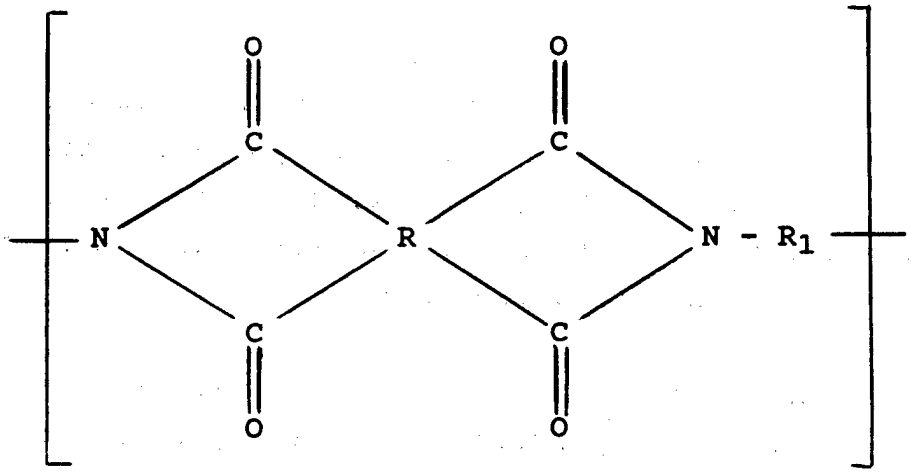
In addition to your elaborated solution, you may - but this is not mandatory - give, on a separate sheet of paper, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such statement should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such a request when enrolling for the examination - give their answer in a language other than German, English or French.

Description of the Application

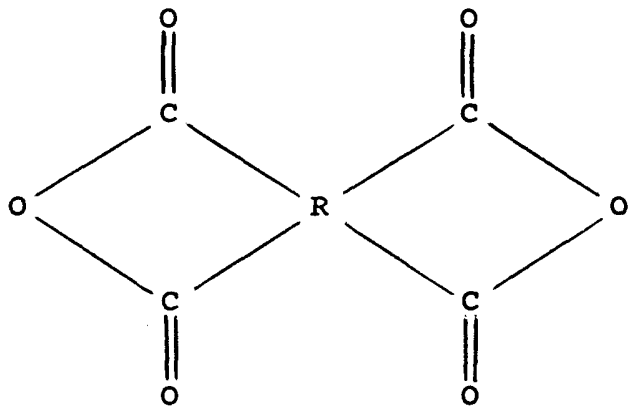
Process for the preparation of Polyimides and shaped articles produced therefrom

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 R_1 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 $H_2N - R_1 - NH_2$, wherein R_1 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 object of the invention is to develop a process that does not have these drawbacks.

The problem is solved according to the invention 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. The formation of 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 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.

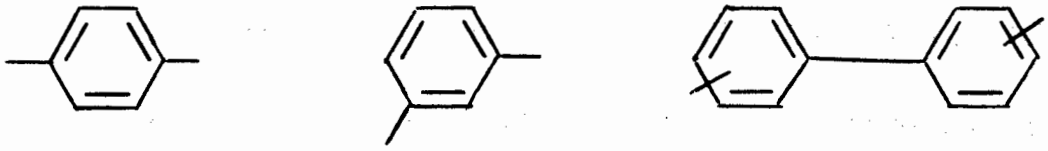
Moulding may take place as soon as the reaction mixture has been partly converted into polyamide acid, for example as soon as a conversion of the reaction mixture of 50% has been achieved.

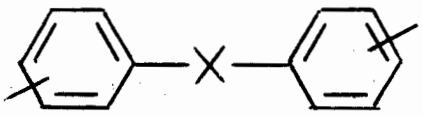
To produce the polyamide acid, approximately equimolar amounts of the said diamine and the dianhydride are mixed as dry solids. The mixture obtained is then added, in small proportions and with

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.

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 al 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.

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 using the process of 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 flexible and tear-resistant.

According to another procedure, a solution of polyamide acid 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.

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 semipermeable 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.

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

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 reac with the acid anhydride a polyamide acid solution with a polym 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, 17 g, 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 peri 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, 10 g, 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, 16 g, and pyromellitic acid dianhydride, 18 g, 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, 16 g, 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

Claims

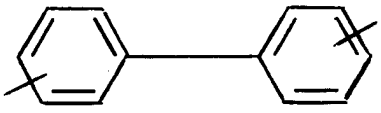
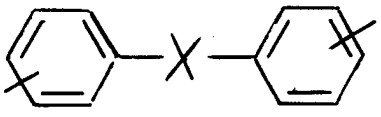
1. A process for preparing polyimides, in which a diamine of the structural formula $H_2N-R_1-NH_2$, wherein R_1 is a divalent radical containing at least one aromatic ring, is reacted with a dianhydride of an aromatic tetracarboxylic acid in an organic polar solvent at a temperature of between 20°C and 120°C until a polyamide acid intermediate product has formed which is then converted to polyimide, **characterised in that** the conversion of the polyamide acid into polyimide is carried out by treatment of the polyamide acid with an anhydride of a lower aliphatic monocarboxylic acid.

2. A process as claimed in claim 1, **characterised in that** as the anhydride of the lower aliphatic monocarboxylic acid acetic acid anhydride is used.

3. A process as claimed in claims 1 or 2, **characterised in that** the polyamide acid is treated with an anhydride of a lower aliphatic monocarboxylic acid in the presence of a tertiary amine.

4. A process as claimed in claim 1, **characterised in that** as the dianhydride of the aromatic tetracarboxylic acid pyromellitic acid dianhydride or benzophenone tetracarboxylic acid dianhydride is used.

5. A process as claimed in claim 1, **characterised in that** the diamine corresponding to the structural formula $H_2N-R_1-NH_2$ is one in which R_1 is

 or 

and X is an alkyl group having 1 to 3 carbon atoms, sulphur, SO_2 or oxygen.

6. A process as claimed in claim 1, characterised in that a polar organic solvent N,N-dimethylformamide or N,N-dimethylacetamide is used.

7. A process as claimed in any one of claims 1 to 6, characterised in that equimolar amounts of the diamine and the dianhydride are used.

8. A process for preparing shaped articles of polyimide, characterised in that the polyamide acid intermediate product obtained according to claims 1 to 7 is moulded into the required shape prior to treatment with the anhydride of the lower aliphatic monocarboxylic acid or with a mixture containing said anhydride.

9. A process as claimed in claim 8, characterised in that the shaped structure is a self-supporting film or sheet.

Communication

1. It is already known from Document III that a polyamide ac obtained by reacting an aromatic diamine with a dianhydride an aromatic carboxylic acid in an organic solvent can be converted to a polyimide by treatment with a dehydrating agent. Acetic acid anhydride is described in particular as a dehydrating agent (see the Example in Document III). The process as claimed in claim 1 is therefore not novel, and hence claim 1 is not allowable, Art. 54 (1) and (2) EPC.

2. According to Document III pyromellitic acid dianhydride in particular is used for the preparation of the polyamide acid while, for example, 4,4'-diamino-diphenyl ether is used as the diamine. A suitable organic solvent according to Document III is N,N-dimethylformamide. Accordingly claims 2, 4, 5 and 6 are not allowable either, due to lack of novelty.

3. Document III does not explicitly mention the use of the reactants in the quantitative ratio referred to in claim 7. Given the nature of the reaction between the anhydride and the amine, each with 2 reactive groups, the feature of claim 7 seems trivial. Therefore claim 7 is not allowable in view of Art. 56 EPC.

4. Claims 8 and 9 are not allowable either, as they are anticipated by Document III.

5. Document IV is considered to be relevant to claim 3. this document teaches that the dehydration of the polyamide acid and the resulting conversion to polyimide is promoted to a considerable degree by the presence of a tertiary amine, in particular pyridine. Although in the process described in

Document IV conversion takes place in the absence of a dehydrating agent, the teaching is directly transferable to the chemical method according to claim 3; hence the process of claim 3 does not involve an inventive step and this claim is not allowable either, Art. 56 EPC.

6. Apart from the above objections, claim 1 does not meet the requirements of Art. 84 EPC since the term "lower" in the definition of the carboxylic anhydrides added during the cyclisation reaction is vague.

7. If revised claims are filed, you are requested to bring the description into agreement with the new claims and also to insert a correct acknowledgement of the prior art, Rule 27(1)(c) and (d) EPC.

Document III (State of the Art)

The invention relates to a process for preparing polyimides by reacting an aromatic diamine with an aromatic tetracarboxylic acid dianhydride and by subsequent dehydration of the polyamide acid so obtained.

The reaction is carried out in an organic solvent at a temperature below 120°C until the reactants have been at least 50% converted to polyamide acid. The organic solvent selected must be capable of dissolving the polyamide acid obtained, thus producing a solution of relatively high viscosity.

As polyimides are difficult to mould once formed, the polyamide acid is then shaped as required, in particular into a film or fibre. It can subsequently be converted to polyimide in various ways, either by heat treatment or by a chemical route.

To prepare the polyamide acid the diamine, preferably in solid form, is mixed with the tetracarboxylic acid dianhydride, and the mixture is gradually added portionwise and with continuous stirring to the organic solvent. In this way both temperature and the progress of the chemical reaction can be correctly controlled. Alternatively, the two reactants can be dissolved first and then mixed.

The aromatic diamines used in particular are 4,4'-diamino-diphenyl ether and 4,4'-diamino-diphenyl propane.

Examples of suitable aromatic tetracarboxylic acid dianhydrides are pyromellitic acid dianhydride, 2,3,6,7-naphthalene tetracarboxylic acid dianhydride and 3,4,3',4'-diphenyl tetracarboxylic acid dianhydride.

The preferred solvents are the organic solvents of the N,N-dialkylcarboxylic acid amide class, in particular

N,N-dimethylformamide. N-Methyl-2-pyrrolidone, dimethyl sulphoxide or N,N-dimethyl methoxyacetamide may also be used.

The above solvents may, if appropriate, be used with other weak solvents such as benzene, toluene and cyclohexane.

To convert the polyamide acid solution into polyimide by heat treatment the solution is heated to between 50 and 150°C for 30 to 60 minutes and then kept at 300 to 500°C for another 5 to 15 minutes.

With the chemical method, conversion to polyimide occurs by treating the polyamide acid with a dehydrating agent, in particular acetic acid anhydride. Other agents such as propionic acid anhydride and butyric acid anhydride may also be used. The polyimide may also be formed by a two-stage method combining a chemical reaction and heat treatment.

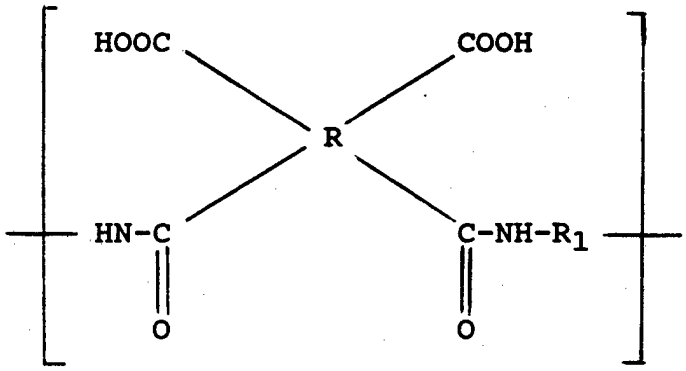
Complete cyclisation to polyimide is carried out preferably only after shaping.

Example

4,4'-Diamino-diphenyl ether, 12.4 g, was mixed with pyromellitic acid dianhydride, 25 g. The mixture was then dissolved in 75 ml of N,N-dimethylformamide with continuous stirring. A viscous solution formed which was diluted with 60 ml of N,N-dimethylformamide. Films were produced by casting the polyamide acid solution on a glass plate. The films were vacuum-dried at 80°C for 30 minutes and separated from the plate. The films were then immersed in a 10:1 mixture of cyclohexane and acetic acid anhydride for 12 hours. The films were then treated with dioxane and dried at 120°C. The films had a modulus of elasticity of 2500 MPa, elongation of 7% and strength of 100 MPa.

Document IV (State of the Art)

The invention relates to a process for preparing polyimide powders by dehydrating solutions or suspensions of polyamide acids with a recurring unit of the general formula



wherein R is a tetravalent radical with at least one aromatic or heteroaromatic ring and R_1 is a divalent radical with at least one aromatic or heteroaromatic ring.

Dehydration according to the invention takes place in the presence of a tertiary amine, in particular pyridine. Trimethylamine and triethylamine can also be used with particularly good results as the tertiary amine.

When these polyamide acids are converted into polyimide, the conversion process is accompanied by hydrolysis, causing degradation of the polymer. The presence of a tertiary amine such as pyridine catalyses the conversion of polyamide acids to polyimide. The ring closure reaction or cyclisation is stepped up

considerably, as a result of which hydrolysis is suppressed. The polyamide acid is converted into the corresponding polyimide at a lower temperature and in a shorter time than without the tertiary amine.

Example

A solution of 0.900 kg of 4,4'-diamino-diphenyl ether in 5.3 kg of dimethylacetamide is added to a solution of 1.250 kg of pyromellitic acid anhydride in 10.2 kg of dimethylacetamide. The mixture is kept at 35°C for 1 hour with stirring. A viscous solution of polyamide acid is gradually formed. This solution is then put into a vessel containing anhydrous pyridine under reflux. The entire mixture is heated to 145°C and refluxed for 80 minutes. After 15 minutes yellow polyimide begins to precipitate out, and a polyimide suspension is formed. At the end of the heating period the product is filtered off, purified by washing with acetone and dried in a vacuum oven at 60°C. The dry polyimide powder is then heat-treated at 325°C under nitrogen for 10 hours prior to processing. From this a solid disc is formed at 400°C and under pressure of 2100 N/cm^2.