

The present invention relates to the use of polyamide-carboxylic acids which are employed as intermediate products for the preparation of electrically insulating high-temperature resistant layers of polyimides. The polyimide layers serve, in particular, as protective layers and insulating intermediate layers for electronic components and circuits on semi-conductors or metals.

The use of polyimides for high-temperature resistant layers on and in semi-conductor devices is known, for example, from DE-B 17 64 977. The polyimides are prepared by polycondensation of aromatic diamines, for example, 4,4'-diamino-diphenyl ether, with aromatic tetracarboxylic acid anhydrides, for example, pyromellitic dianhydride, to give polyamide-carboxylic acids and heating of the polyamide-acids, whereby the polyimide forms with splitting off water. These polyimides have the required temperature resistance and the desired electrical properties, if their molecular weights are high enough. The solutions of the corresponding high-molecular weight polyamide-carboxylic acids, however, have a high viscosity, already at relatively low concentrations. They are therefore processed with difficulty. The high-molecular weight polyimides as such are usually relatively brittle and can only insufficiently planarize, i.e. embed in a layer having a plane surface, the conductive paths covered by them.

A reduced viscosity at an unchanged molecular weight is obtained, when pyromellitic acid is entirely or partly replaced by benzophenone-3,3',4,4'-tetracarboxylic acid. Polyamide-carboxylic acids of that type and polyimides prepared therefrom are described in DE-B 15 20 767. In the publication "Pyralin, Polyimide Coatings for Electronics", Bulletin PC-1 of E.I. du Pont

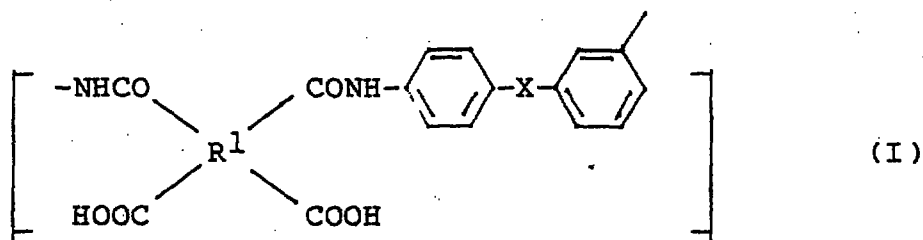
de Nemours and Co., Wilmington, U.S.A., the improved planarizing effect of these polyimides is pointed out. The corresponding polyamide-carboxylic acids, however, tend to enter into cross-linking reactions to form insoluble products, already at relatively low temperatures. The processing range of these intermediate products is therefore limited. This disadvantage is the more pronounced, the higher the proportion of benzophenone-tetracarboxylic acid units; the reduction in viscosity, which can practically be achieved, is thus limited. In addition, the thermal stability of polyimides based on pyromellitic acid derivatives is generally higher than the thermal stability of polyimides prepared from benzophenone-tetracarboxylic acid derivatives.

The diamine components of the polyamide-carboxylic acids have also been varied, but particular changes of properties in connection therewith have not been described. For example, in US-A 3,179,614, phenylene diamines, naphthylene diamines, xylylene diamines, substituted benzidines, diamino-pyridines and diamino-diphenyl ethers, -diphenyl sulfides, -diphenyl sulfones, -diphenyl methanes and -benzophenones are enumerated as the diamine components. In addition to the 4,4'-isomers of the binuclear compounds, which are mentioned in the first place, this patent also specifies 3,3'-diamino-diphenyl sulfone and 3,4'-diamino-biphenyl. Examples of application are only given for the 4,4'-isomers.

EP-A 0 179 604 describes polyamide-carboxylic acids and polyimides prepared therefrom, which contain, as the diamine components, 3,3'-, 4,4'- and 3,4'-isomers and are employed in the form of powders for the preparation of adhesives.

It is an object of this invention to provide solutions of polyamide-carboxylic acids which, at a molecular weight corresponding to that of known compounds of the same type, exhibit a lower viscosity in solution and result in polyimides which produce an improved planarization, without giving rise to any loss in processing range.

According to the invention solutions of polyamide-carboxylic acids are provided, which are used for coating semiconductor components and comprise at least 50 mole-% of recurrent units of the general formula I



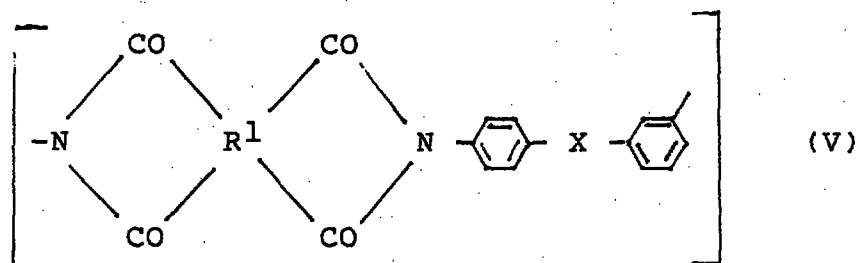
and contain, on an average, 2 to 400 of these units, wherein

R^1 is a mono-to tetranuclear aromatic group and

X is O, S, CO, SO_2 or CR^2R^3 ,

R^2 and R^3 being identical or different and denoting H or CH_3 .

The polyimides prepared therefrom contain at least 50 mole-% of recurrent units of the general formula V



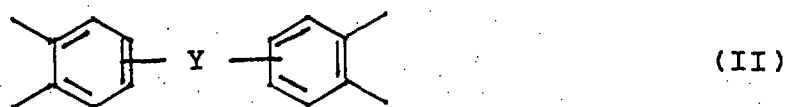
wherein R^1 and X have the above-indicated signification.

For preparing the planarising layer the solution of the polyamide-carboxylic acid is applied to the surface to be coated, the resulting polyamide-carboxylic acid layer is dried by heating to a temperature in the range from 180 to 400 °C, with a polyimide forming in the process.

The polyamide-carboxylic acids used according to the present invention contain, on an average, 2 to 400, preferably 20 to 200, units of formula I.

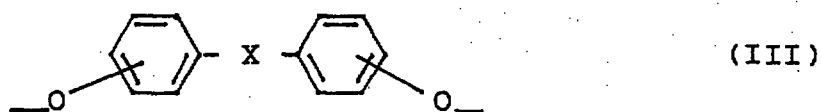
If R^1 in formula I contains more than one aromatic ring, these rings are linked to one another preferably by single bonds or substituents. R^1 can, in particular, be a phen-1,2,4,5-tetrayl group or a group of the formula II

- 5 -



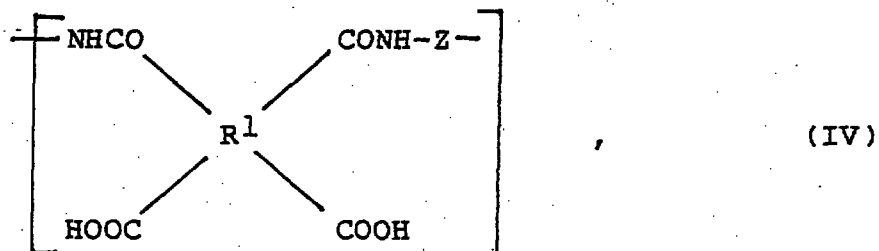
in which

Y is a single bond, a group having the significance of X or a group of the formula III



X having the above-indicated signification.

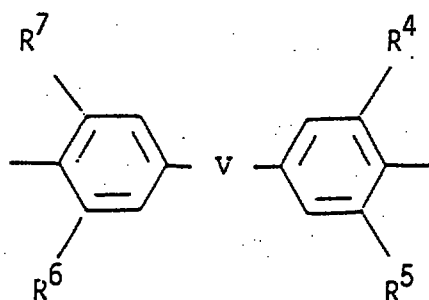
In addition to the units of formula I, the polyamide acids used according to the invention may contain other units formed from tetracarboxylic acids and diamines, which are based on the same tetracarboxylic acids and different diamines, in particular, units of the formula IV



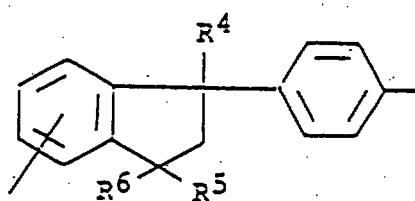
- 6 -

wherein

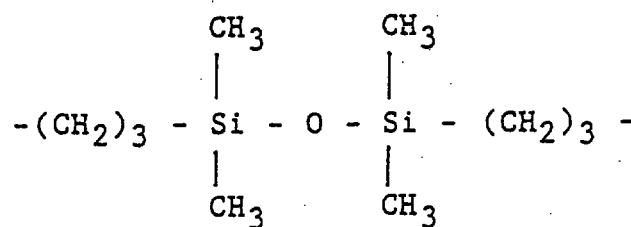
Z is a group of the formula



a group of the formula



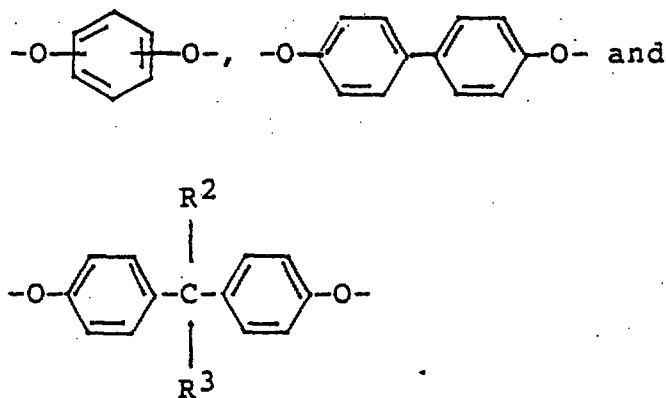
a phenylene group, a naphthylene group or a group of the formula



- 7 -

R^4 , R^5 ,
 R^6 and R^7 being identical or different and denoting hydrogen atoms or alkyl groups having from 1 to 3 carbon atoms and

V being a single bond or a group having the signification of X or one of the groups



The corresponding copolymers may contain up to 50 mole-%, preferably not more than 30 mole-%, of units of the formula IV. Within a single polyamide-acid, units derived from different tetracarboxylic acids and different diamines may be present.

In the general formulae, R^1 preferably is a mono- or binuclear aromatic group. X preferably is CO, CR^2R^3 or O, especially O.

The polyamide-carboxylic acids used according to this invention are prepared in analogy to known processes, as follows:

In an inert gas atmosphere, the diamine compound is dissolved with stirring in an inert solvent which is free of water and amines.

Preferably used inert solvents are those which dissolve the intermediate product of the polyamide-acid type formed, for example, N-methylpyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, dimethylsulfoxide, hexamethylphosphoric acid triamide, tetramethylensulfone and N-methylpiperidone. It is possible to use these solvents individually, in combination with each other or in combination with non-solvents, such as benzene, benzonitrile, dioxane, butyrolactone, xylene, toluene, cyclohexane, 2-methoxy-ethanol, acetone and propylene glycol monomethyl ether.

The solution is kept at a temperature below 30 °C by external cooling, while adding the tetracarboxylic acid dianhydride. The resulting mixture is stirred until the tetracarboxylic acid dianhydride has completely dissolved. In the process, the viscosity of the reaction system rises, while the polyamide-carboxylic acid is formed.

When preparing polyamide-carboxylic acids with defined molecular weights from the tetracarboxylic acid dianhydrides and diamines it is necessary that the monomers are of maximum purity. The monomers are preferably purified prior to the reaction process by recrystallization, sublimation, distillation, melt crystallization or zone refining. It is also necessary to use the tetracarboxylic acid dianhydride with substantially equimolar quantities of diamine (tolerance below ± 5 mole-%). Pre-

ferably a slight excess of diamine compound of approximately 1 to 3 mole-% is employed.

The resulting polyamide-carboxylic acid solutions have solids contents ranging from 6 to 45 %, preferably from 10 to 30 % and viscosities ranging from 500 to 10,000 mPa·s, preferably from 800 to 7,000 mPa·s. The inherent viscosity of the polymers is at least 0.1 dl/g, preferably 0.3 to 1.5 dl/g. The inherent viscosity is defined as follows:

$$\eta_{inh.} = \frac{\ln \frac{\eta_{solution}}{\eta_{solvent}}}{c}$$

c being the concentration in grams of polymer per 100 ml of solution. The viscosity of the polymers according to the present invention is, in each case, measured at 25 °C on an 0.5 % strength solution in N-methylpyrrolidone.

Below the invention is explained in detail by examples of application and reference examples.

Example 1

a) In a 500 ml reaction vessel equipped with thermometer and stirrer 12.5 g (0.0625 mole) of distilled 3,4'-diamino-diphenyl ether and 100 g of N-methylpyrrolidone were placed under a nitrogen atmosphere and the mixture was vigorously stirred until the diamine had completely dissolved. The reaction vessel had a cooling jacket through which water circulated. 13.4 g (0.0614

mole) of recrystallized pyromellitic dianhydride in coarse lumps were added to the solution at one time. The reaction mixture was rinsed with 133 g of N-methylpyrrolidone and stirred until the tetracarboxylic acid anhydride had completely dissolved. In the reaction taking place, a solution was obtained which contained 10 % by weight of polyamide acid. The solution had a viscosity of 194 mPa·s at 25 °C, the value calculated for the inherent viscosity was 0.78 dl/g.

b) A polyamide acid solution prepared according to the procedure described under (a) above, from 12.5 g of 3,4'-diamino-diphenyl ether and 13.4 g of pyromellitic dianhydride, which contained 17 % of resin, had a viscosity of 2,420 mPa·s at 25 °C and an inherent viscosity of 0.79 dl/g.

c) (Reference)

A solution prepared according to the procedure described under (a) above, from 12.5 g of 4,4'-diamino-diphenyl ether and 13.4 g of pyromellitic dianhydride, which contained 10 % of polyamide acid, had a viscosity of 2,150 mPa·s at 25 °C and an inherent viscosity of 1.33 dl/g.

Example 2

a) According to the procedure described in Example 1(a), 12.5 g (0.0625 mole) of 3,4'-diamino-diphenyl ether were reacted with 19.8 g (0.0614 mole) of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride in 291 g of N-methylpyrrolidone. The resulting solution which contained 10 % of polyamide acid had a viscosity of 98 mPa·s at 25 °C and an inherent viscosity of 0.64 dl/g.

- 11 -

b) A 17 % strength polyamide acid solution prepared according to the procedure described in Example 1(a), from 12.5 g of 3,4'-diamino-diphenyl ether and 19.8 g of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride, had a viscosity of 376 mPa·s at 25 °C and an inherent viscosity of 0.63 dl/g.

c) (Reference)

According to the procedure described in Example 1(a), 12.5 g of 4,4'-diamino-diphenyl ether were reacted with 19.8 g of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride in 291 g of N-methylpyrrolidone. The resulting solution which contained 10 % of polyamide acid had a viscosity of 376 mPa·s at 25 °C and an inherent viscosity of 0.95 dl/g.

Example 3

According to the procedure described in Example 1(a), a mixture of 75 g (0.0375 mole) of 4,4'-diamino-diphenyl ether and 17.5 g (0.0875 mole) of 3,4'-diamino-diphenyl ether was reacted with 26.9 g (0.123 mole) of pyromellitic dianhydride in 468 g of N-methylpyrrolidone. The resulting solution which contained 10 % of polyamide acid had a viscosity of 480 mPa·s at 25 °C and an inherent viscosity of 0.98 dl/g.

Example 4

a) The lacquer obtained in Example 1(a) was cast onto a glass plate to produce a coating on the plate. The coated plate was heated for 2 hours at 100 °C and, as a result, a 40 to 50 µm thick film was formed. The film was again heated for 1 hour at 220 °C and then for 1 hour at 350 °C.

- 12 -

With the aid of a differential thermobalance, the temperature at which weight loss started was determined at 450 °C; the rate of weight loss determined in an air stream at 455 °C was 18.4 %/h.

b) A film was prepared as described under (a) above, using the lacquer obtained in Reference Example 1(c). The temperature at which weight loss started was determined at 450 °C; the rate of weight loss determined in an air stream at 458 °C was 16.4 %/h. This result shows that the polymers of the present invention practically have the same temperature resistance as the isomeric compounds known in the art.

Example 5

a) A transistor equipped with an aluminum electrode was coated with the lacquer obtained in Example 1(a). Then the transistor was heated for 1 hour at 100 °C and for another hour at 220 °C. After masking with photoresist, the area directly above the aluminum electrode was etched with hydrazine, followed by heating for 1 hour at 350 °C. Thereafter aluminum was vacuum-deposited such that a double-layer structure resulted. The current transfer ratio [change of h_{FE} -linearity = (h_{FE} -linearity after treatment at 520 °C) - (h_{FE} -linearity prior to heat treatment)] of the transistor thus obtained was +0.3 %.

b) (Reference)

A transistor having a double-layer structure was prepared as described under (a) above, using the lacquer obtained in Example 1(c) (Reference). The current transfer ratio of the transistor was +0.3 %.

- 13 -

As shown by the results of Example 5, it has no effect on the electrical properties of a transistor whether it is coated with customary polyimides derived from 4,4'-diamino-diphenyl ether or with the polyimides of the present invention which are derived from 3,4'-diamino-diphenyl ether.

Example 6

a) Silicon dioxide lines being 0.9 μm high and 3 μm wide and spaced 7 μm on a silicon wafer were spin-coated at 5,000 rpm with a layer of the lacquer obtained in Example 1(b). The lacquer was then heated for one hour at 250 °C and for another hour at 350 °C. The degree of planarization (see L.B. Rothman, J. Electrochem. Soc. 127, 2216-20 (1980)) was 50 %.

b) (Reference)

A wafer carrying silicon dioxide lines as under (a) was spin-coated at 5,000 rpm with a layer of the lacquer obtained in Example 1(c). After heat treatment the degree of planarization was 29 %.

As can be seen from the above description, solutions of intermediate products of the polyamide-acid type which, from the point of view of processing technique, have more favorable properties (reduced viscosity at a higher solids content) are available, when replacing the usually employed 4,4'-diamino-diphenyl ether by 3,4'-diamino-diphenyl ether. The novel intermediate products of the polyamide-acid type have the same good electrical and thermal properties and considerably improved planarization properties.

- 14 -

Example 7

The surface of a silicon wafer which was covered with a first patterned layer of aluminum conductors was spin-coated with the polyamide-carboxylic acid solution obtained according to Example 1(a). The solution was dried and heated for 1 hour at 130 °C. A commercial positive photoresist solution based on naphthoquinone di-azides and novolaks was applied to the still uncured polyamide-acid layer, the photoresist was dried, exposed and developed with a commercial aqueous-alkaline developer solution. In the development process, the photoresist layer and also the underlying polyamide-acid layer were removed in the exposed areas and the surface of the aluminum layer was uncovered. The photoresist stencil was then removed with acetone and the polyamide-carboxylic acid layer was cured for 1 hour at 350 °C.

The polyimide stencil obtained covered the aluminum conductors and only the desired contact points were left free. On the entire surface a second aluminum layer was vacuum-deposited and structured to form a layer of conductors in the usual manner by a photolithographic process.

Example 8

This example shows the use according to the invention of a polyimide as a protective layer on the surface of a transistor, which prevents contaminants from penetrating.

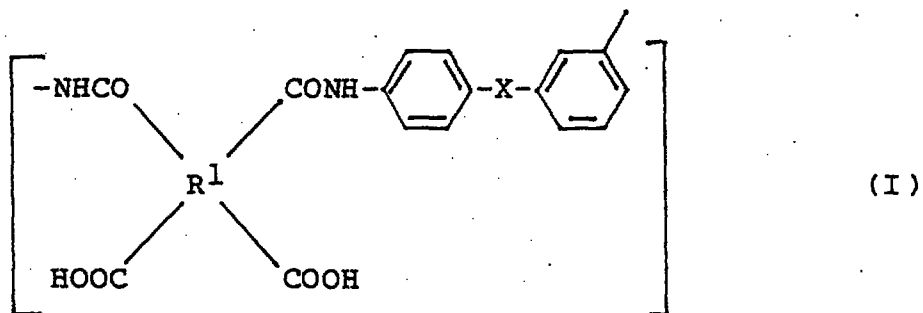
A transistor with laterally disposed contacts, produced on a silicon wafer in a known manner was coated

- 15 -

with a polyamide-carboxylic acid layer according to Example 2(b). The layer was dried, heated for one hour at 100 °C and for another hour at 220 °C. The resulting polyimide layer was spin-coated with a commercial negative-working photoresist solution and dried. The photoresist layer was exposed under an original, in which the contact points only were covered. By developing, the polyimide layer, which is insoluble in the developer, was uncovered at these points and then etched with hydrazine. The photoresist stencil was removed and the polyimide layer cured for 1 hour at 350 °C. A transistor was obtained, the surface of which was protected by the polyimide layer, with the exception of the contact points.

CLAIMS

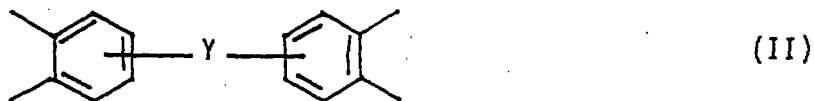
1. Use of a solution of polyamide-carboxylic acids for coating semiconductor components, wherein the polyamide-carboxylic acids comprise at least 50 mole-% of recurrent units of the general formula I



and contain, on an average, 2 to 400 of these units, wherein

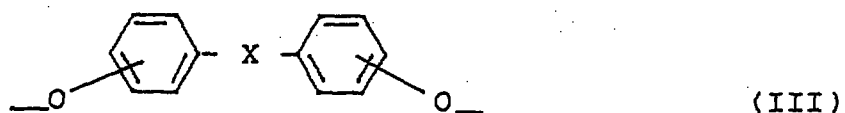
R¹ is a mono- to tetranuclear aromatic group and
X is O, S, CO, SO₂ or CR²R³,
R² and R³ being identical or different and denoting H
or CH₃.

2. Use as claimed in claim 1, wherein
R¹ is a phen-1,2,4,5-tetrayl group or a group of the
formula II



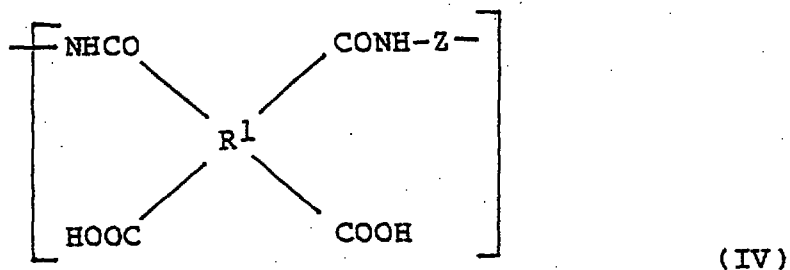
wherein

Y is a single bond, a group having the signification of X or a group of the formula III



X having the signification indicated in claim 1.

3. Use as claimed in claim 1 or 2, wherein the polyamide carboxylic acids additionally contain units of the formula IV

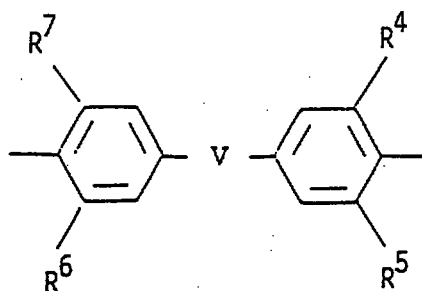


wherein

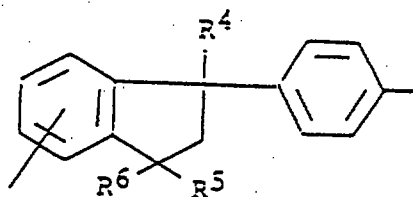
Z is a group of the formula



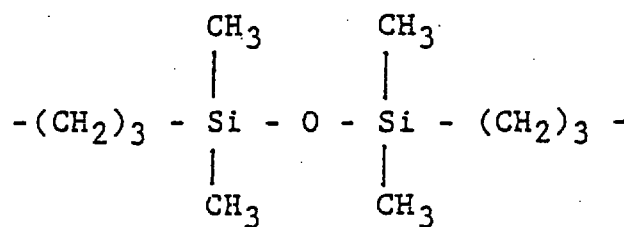
- 18 -



a group of the formula

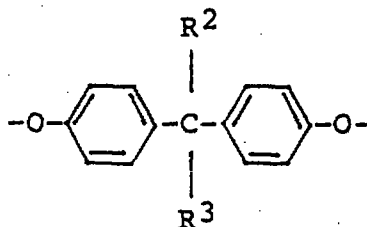
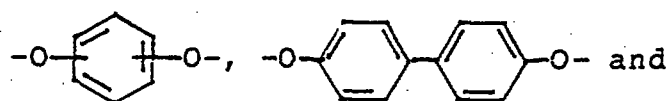


a phenylene group, a naphthylene group or a group of the formula



- 19 -

R^4, R^5 , being identical or different and
 R^6 and R^7 denoting hydrogen atoms or alkyl groups
 having from 1 to 3 carbon atoms and
 V being a single bond, a group having the
 signification of X or one of the groups



4. Use as claimed in any of claims 1 to 3,
 wherein the solvents used are free of water and amines.

5. Use as claimed in any of claims 1 to 4,
 wherein the solvent used comprises N-methylpyrrolidone,
 N,N-dimethylacetamide, N,N-dimethylformamide, N,N-di-
 ethylformamide, dimethylsulfoxide, hexamethylphosphoric
 acid triamide, tetramethylenesulfone and N-methylpiperi-
 done or a mixture of these.

6. Use as claimed in any of claims 1 to 5,
 wherein the solvent used comprises a solvent mixture of
 one or more of the solvents of claim 5 in combination
 with a non-solvent.



- 20 -

7. Use as claimed in claim 6, wherein the solvent mixture contains as non-solvents compounds such as benzene, benzonitrile, dioxane, butyrolactone, xylene, toluene, cyclohexane, 2-methoxy-ethanol, acetone or propylene glycol monomethyl ether.

8. Use as claimed in any of claims 1 to 7, wherein the solution has a solids content of 6 to 45 % by weight, preferably of 10 to 30 % by weight.

9. Use as claimed in any of claims 1 to 8, wherein the solution has a viscosity of 500 to 10,000 mPs·s, preferably of 800 to 7,000 mPs·s.

10. Use as claimed in any of claims 1 to 9, wherein the polymer contained in the solution has an inherent viscosity of at least 0.1 dl/g, preferably of 0.3 to 1.5 dl/g.

-.-.-

to form polycondensates and/or
be added to the polymer solution
and/or to the polymer solution
and/or to the polymer solution
and/or to the polymer solution



* C L N S *