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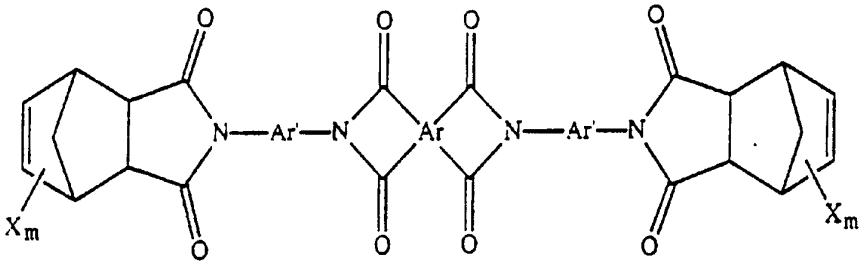

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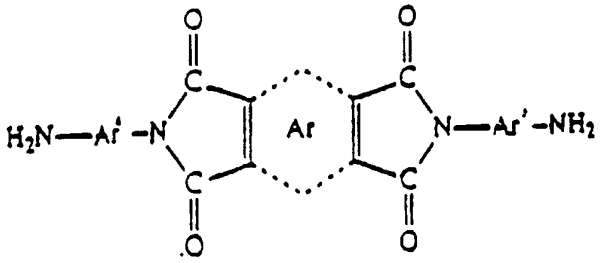

(III)

(57) Abstract

The invention relates to a method for the preparation of a bisnadimide of formula (II) substantially free of oligomeric, amidic and uncyclized impurities wherein: Ar is an optionally substituted aryl, optionally substituted bridged or bonded di- or poly- aryl or optionally substituted heteroaryl group; Ar' is an optionally substituted aryl or heteroaryl group which provides for good conjugation between the nitrogen containing groups; X is hydrogen, halogen or an alkyl group; and m is 0 to 6 which comprises reacting a diaminobisimide of formula (III); wherein Ar and Ar' are as defined in formula (II) with nadic acid or a reactive derivative thereof which is optionally substituted with an alkyl group. The invention also relates to bisnadimides of formula (II) and high temperature resistant matrix polymers for composites made therefrom.

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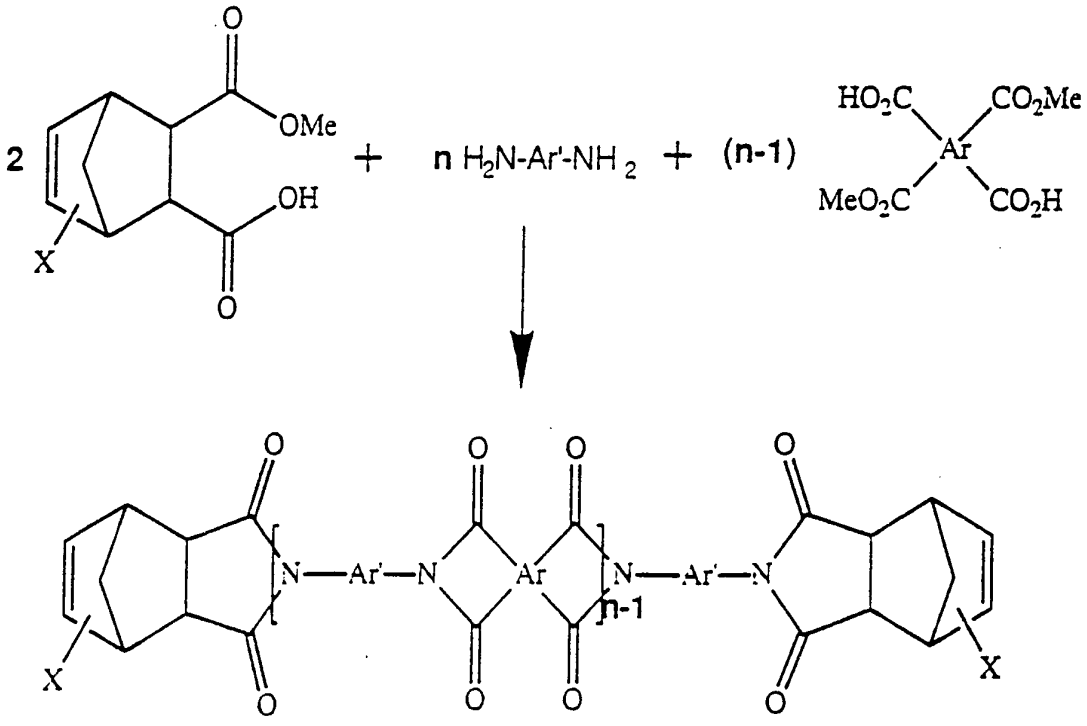
BISNADIMIDES

The invention is concerned with bisnadimides and polymers, particularly high temperature resistant matrix polymers for composites, made therefrom.

In recent years the most practical of the high temperature thermostable polyimide matrix resins developed for the aerospace industry has been the Polymerizable Monomeric Reactants (PMR)-type, produced by workers in NASA, USA. These resins are monomeric mixtures of aromatic diamines with nadic anhydride and aromatic dianhydride based esters. These mixtures were reported to react at intermediate temperatures to give nadimide capped oligomers of Formula (I) as shown below.



Formula (I)

At higher cure temperatures, these oligomers melt and crosslink to form a continuous stable matrix in advanced composite structures. Recent work (J.N. Hay, J.D. Boyle, P.G. James, J.R. Walton, and D. Wilson, "Polymerisation Mechanisms in PMR 15 Polyimide,", in *Polyimides: Materials, Chemistry and Characterization*, C. Feger, M.M. Khojasteh, and J.E. McGrath Eds., Elsevier, Amsterdam, 1989, pages 305 to 320) has shown that the oligomers formed have much more complex structures with unreacted ester and acid groups as well as uncyclized structures. This complexity and partial reaction means that consistent resin properties are not possible and also lead to brittleness, microcracking and voids in the final composites. The aromatic diamine monomers present in the resins often have toxicity and stability problems, for example, diaminodiphenylmethane - the most commonly used aromatic diamine in industry.

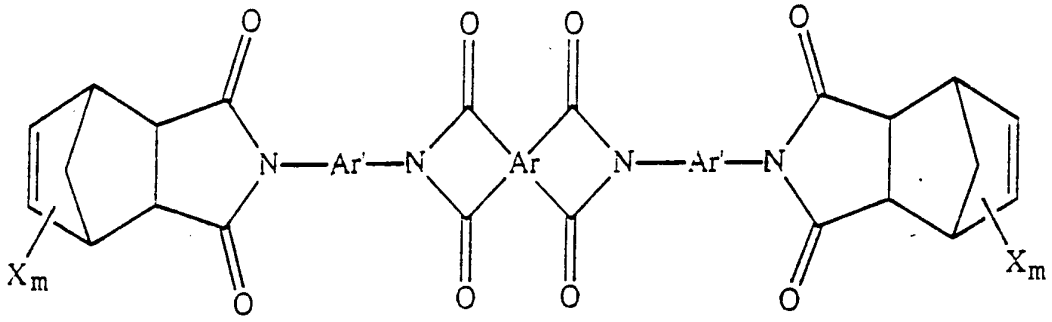
An alternative approach to improve composite toughness, etc., has been to use higher molecular weight or fluorinated monomers in the initial resin mixtures and hence improve molecular mobility and processability. The difficult challenge however is to prepare relatively homogeneous materials without increasing material costs greatly.

International Patent Publication No. WO 92/06078 by the present applicant which is incorporated herein by reference describes a process for the low cost production of novel, high molecular weight monomeric diaminobisimides (hereinafter referred to as "DABIs") of well defined structure and substantially free of oligomeric, amidic and uncyclized impurities. These aromatic diamines have also been found to be non-toxic and stable. International Patent Publication No. WO 92/06078 also discloses the use of DABIs as hardeners for epoxy resins.

In European Patent Publication No. 0 479 722 A2, Kramer *et al* disclose oligomeric polyimides of Formula (I) as defined above wherein Ar is C_6H_2 and $5<n<150$. These polyimides are stated to be soluble and useful as tougheners in crosslinked resin systems.

We have now found that DABIs produced by the process disclosed in International Patent Publication No. WO 92/06078 can be used to make bisnadimides which crosslink on heating to give thermally stable polyimide resins having superior properties.

According to one aspect of the present invention there is provided a method for the preparation of a bisnadimide of Formula (II) substantially free of oligomeric, amidic and uncyclized impurities



Formula (II)

wherein

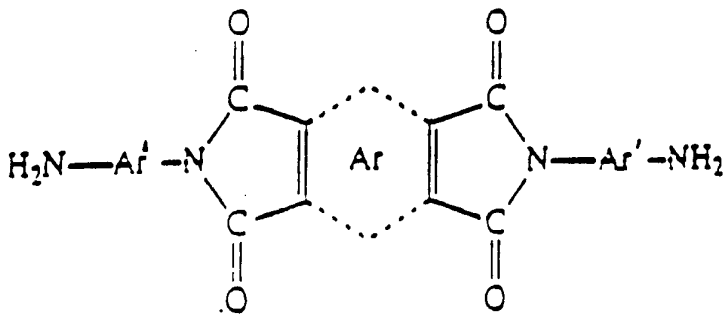
Ar is an optionally substituted aryl, optionally substituted bridged or bonded di- or poly- aryl or optionally substituted heteroaryl group;

Ar' is an optionally substituted aryl or heteroaryl group which provides for good conjugation between the nitrogen containing groups;

X is hydrogen, halogen or an alkyl group; and

m is 0 to 6

which comprises reacting a diaminobisimide of the Formula (III)



Formula (III)

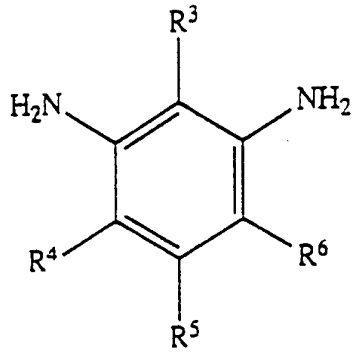
wherein Ar and Ar' are as defined in Formula (II) above with nadic acid or a reactive derivative thereof which is optionally substituted with an alkyl group.

As used herein the term "good conjugation" means that during formation of the diaminobisimide precursor from a diamine of Formula (IV) shown below, substitution of an electron-withdrawing group on one of the nitrogen atoms suppresses the reactivity of the other nitrogen atom during the reaction.

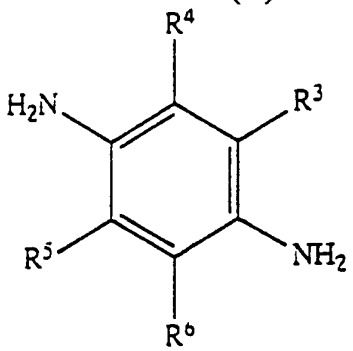
$H_2N\text{-}Ar'\text{-}NH_2$

Formula (IV)

Preferably the aromatic diamine of the Formula (IV) is sterically hindered, such as in compounds of Formulae (V) and (VI)



Formula (V)



Formula (VI)

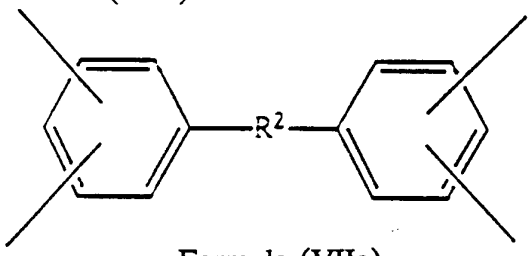
wherein R^3, R^4, R^5 and R^6 are the same or different and each may be selected from alkyl, aryl, heteroaryl, nitro and halogen groups.

Ar or Ar′ may be substituted with one or more alkyl, alkoxy, alkylthio, aryl, heteroaryl, aryloxy, carboxy, alkylthio, alkylamino, dialkylamino, amino, nitro, cyano or halo groups.

"Aryl" means an aromatic carbocylic group, such as phenyl, naphthyl, and the like.

"Bridged or bonded di- or poly- aryl" means a group consisting of two or more aromatic carboxylic ring systems, such as phenyl, naphthyl or the like joined by a bond, such as in biphenyl, or a bridging group, such as in sulphonyldiphenyl.

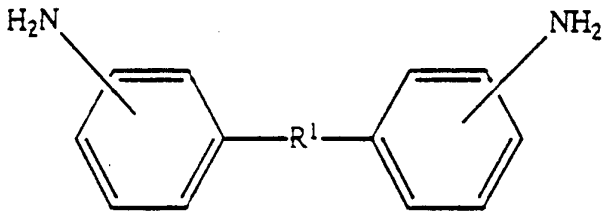
"Bridging group" includes for example SO_2, CO, CH_2 and O such as in compounds of the Formula (VIIa)



Formula (VIIa)

wherein R^2 is a divalent group such as $-SO_2-$, -CO-, $-CH_2-$ and -O-.

Generally the group Ar′ may be selected from the groups listed above for Ar. However, because of the constraints imposed by the requirement of "good conjugation" (as defined above) some bridged di- or poly- aryl groups may not be suitable. Thus for Ar′, the bridging group (if present) must provide good conjugation between the amino groups of the diamine moiety (IV). For example in groups of the Formula (VIIb)



Formula (VIIb)

wherein R^1 is CH_2 or where the diamine is 3,3'-sulphonyldianiline, there is insufficient conjugation and oligomeric diaminoimides are present in the precursor diaminobisimides. In contrast, benzidine and 4,4'-sulphonyldianilines have sufficient conjugation and give the desired predominantly monomeric diaminobisimide compound and hence a substantially monomeric bisnadimide.

"Heteroaryl" means aromatic monocyclic or polycyclic groups containing at least one heteroatom such as nitrogen, oxygen or sulfur. Examples of suitable "heteroaryl" groups are: 3- to 8- membered, more preferably 5- or 6- membered heteromonocyclic groups containing 1 to 4 nitrogen atom(s), for example, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, triazinyl; condensed heterocyclic groups containing 1 to 5 nitrogen atom(s), for example, indolyl, isoindolyl, indolizinyl, benzimidazolyl, quinolyl, isoquinolyl, indazolyl, benzotriazolyl, etc.; 3- to 8- membered heteromonocyclic groups containing 1 or 2 sulfur atom(s) and 1 to 3 nitrogen atom(s), for example, thiazolyl, isothiazolyl, thiadiazolyl, etc.; 3- to 8- membered heteromonocyclic groups containing 1 to 2 sulfur atom(s), for example thienyl, etc.; condensed heterocyclic groups containing 1 to 2 sulfur atom(s) and 1 to 3 nitrogen atom(s), for example, benzothiazolyl; benzothiadiazolyl, etc.; 3 to 8- membered heteromonocyclic groups containing an oxygen atom, for example, furyl, etc.; condensed heterocyclic groups containing 1 to 2 sulfur atom(s), for example, benzothienyl, etc.; and condensed heterocyclic groups containing 1 or 2 oxygen atom(s), for example, benzofuranyl, etc.

The alkyl group may be straight chain or branched and contain 1 to 20 carbon atoms. Suitable alkyl groups are methyl, ethyl, propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *tert*-butyl, *n*-pentyl, *iso*-pentyl, *neo*-pentyl, *n*-octyl, *iso*-octyl, decyl, cetyl, stearyl, and the like.

"Alkoxy" and "alkylthio" mean groups in which the alkyl moiety is a branched or unbranched saturated hydrocarbon group containing from one to eight carbon

atoms, such as methyl, ethyl, propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *tert*-butyl and the like.

"Alkanoyl" may be formyl, acetyl, propionyl, butyryl, valeryl, *iso*-valeryl, pivaloyl, hexanoyl, and the like.

Preferably, the diaminobisimide of the Formula (III) is produced by the process disclosed in International Patent Publication No. WO 92/06078 as such a compound is substantially free of oligomeric, amidic and uncyclized impurities. However, it will be appreciated that the diaminobisimide of the Formula (III) used in the method of the invention may be produced by any suitable known process.

The reaction is preferably carried out using nadic anhydride or an alkyl-substituted nadic anhydride in the molten state as the solvent.The reaction may also be performed in the presence of a solvent such as an organic solvent, for example, dimethyl formamide, dimethylacetamide or xylene. If a solvent is used, because pure cyclized bisnadimides are formed and can be separated from the solvent as solids, unlike the case in standard PMR type resins, the products can be cured into final resins and composites without the porosity problems caused by strongly bound solvents.

Preferably the reaction is performed at elevated temperatures, such as, for example, above about 120 °C. The method of the invention allows very high yields of substantially pure bisnadimides, even with very insoluble DABIs, to be prepared. Excess optionally substituted nadic anhydride may be removed from the final product by washing with a suitable solvent, such as, for example, ethanol or hot water.

The bisnadimides of Formula (II) are also novel and form another aspect of the present invention.

The invention also provides bisnadimides of Formula (II) whenever prepared by a method as defined above.

The bisnadimides of the invention, which are substantially free of oligomeric, amidic and uncyclized impurities, may be used in a curable formulation to produce impregnated fibre reinforced materials and to form crosslinked polyimide polymers which can be used in advanced composite materials.

By utilising the present invention, the PMR composition containing a toxic, reactive diamine of conventional practice is replaced by a safe, stable bisnadimide which can be readily handled during composite fabrication. Furthermore, on a weight of resin basis, much lower quantities of volatile cyclization products are evolved during the curing step as at least half the groups are already cyclized.

The bisnadimides of the invention can be reacted with or without curing agents to form crosslinked polyimide polymers which are useful for a variety of applications including adhesives, bars, films, electronic encapsulation, moulded components and composites. On curing at elevated temperatures, the bisnadimides of Formula (II) may be converted into crosslinked polyimide polymers having improved properties.

Thus, the invention further provides a curable formulation which comprises a bisnadimide of the Formula (II) as defined above.

The bisnadimides of the invention are particularly useful in the manufacture of fibre reinforced composite materials. For example, curable formulations containing the bisnadimides of the invention may be applied to reinforcing cloth such as uni-directional or woven carbon fibre either from solution (preferably a lower aliphatic ketone or halogenated hydrocarbon solvent) or from a hot melt. Application may be performed manually or by machine and includes techniques involving transfer from a precoated transfer medium.

Therefore, the present invention also provides an impregnated fibre reinforced material (commonly known as a "prepreg") wherein the fibre reinforcements are coated with a curable formulation as defined above.

Thus, according to another aspect of the present invention there is provided a crosslinked polyimide polymer which is formed from a bisnadimide monomer of Formula (II) as defined above.

According to a further aspect of the present invention there is provided a method for the preparation of the crosslinked polyimide polymer defined above which comprises heating a bisnadimide of Formula (II) as defined above.

The bisnadimides are preferably heated to temperatures above about 250 °C. The heating may occur under pressure.

While the prior art describes very few co-reactants for curing PMR type resins, it has been found that trans-stilbene is a particularly good curing additive for the bisnadimides of the invention. Such additives provide cyclizable and aromatizable double bond compounds which are capable of reacting with reactive groups liberated by the bisnadimide type cure. Another additive particularly useful in the production of void-free resin bars from the bisnadimides of the invention is the addition of a small percentage of hydroquinone or other additives to prevent "skinning" and hence entrapment of residual volatiles during the early stages of cure.

The impregnated fibre reinforced material defined above are also suitable for use in the production of advanced composite materials. The impregnated fibre materials may be laid down by any suitable known method for making composite materials, such as, for example, vacuum bagging on a caul plate or an appropriate tool.

Accordingly, the present invention also provides an advanced composite material which comprises an assembly of reinforcing fibres in a matrix of a crosslinked polyimide polymer as defined above.

Alternatively, the bisnadimides of the invention can be used in an appropriate resin formulation for resin transfer moulding or for the manufacture of sheet moulded material. Another envisaged application is in pultrusion.

The invention is illustrated by the following Examples. These Examples are not to be construed as limiting the invention in any way.

The systematic names used in the Examples are based on the Chemical Abstracts names of related compounds.

Example 1

Bisnadimide resin, CBR-116, Formula (II) wherein X is H, Ar is $C_6H_3COC_6H_3$ and Ar' is 1,3 disubstituted methyldiethylphenyl

A mixture of 400g of nadic anhydride and 200g of 5,5'-carbonylbis {2-[3-amino(methyldiethyl)phenyl]}-1H-isoindole-1,3(2H)-dione prepared by the method described in International Patent Publication No. WO 92/06078 were mixed together as finely divided solids and then heated slowly with stirring to 180 °C. The nadic anhydride melted at about 160 °C and dissolved the diamine as well as reacting with it to liberate water. After heating with stirring for 8 hours the toffee-like mixture was cooled, ground and washed with very hot water to remove the large excess of unreacted anhydride.

The remaining solid was dried and then dissolved in the minimum amount of methylene chloride and poured into excess ethanol to give the pure solid bisnadimide as a light brown powder with infrared spectra showing peaks at 1776, 1724, 1710cm^{-1} (imide), 1182, 1106 and 723cm^{-1}.

Example 2

Bisnadimide resin CBR-412, Formula (II) wherein X is CH_3, Ar is C_6H_2 and Ar' is 1,3-disubstituted methyldiethylphenyl

(a) Neat

2,6-bis(3-amino(methyldiethyl)phenyl)-benzo[1,2-c:4,5c']-dipyrrole-1,3,5,7(1H,6H)-tetrone (CBH-103) (2.6g, 0.0049 mole) prepared by the method described in International Patent Publication No. WO 92/06078 was added to liquid methyl nadic anhydride (1.8g, 0.01 mole) and the stirred solution heated at 180 °C for 2 hours and at 200 °C for 2 hours and allowed to cool. The FTIR was consistent with the expected product which was soluble in CH_2Cl_2, acetone, THF and DMF and insoluble in ethanol. The GPC showed one main peak with Mn ≈ 830 (expected value 858). It had no sharp melting point, but softened with decomposition at about 300 °C. Recrystallization from $CHCl_3$/ethanol made no difference to the properties. Curing a sample in the DSC resulted in an endotherm centred at 260 °C, attributed to the retro Diels-Alder reaction, and a broad exotherm commencing at about 300 °C.

(b) In DMF

A solution of CBH-103 (10.7g, 0.02 mole) and methyl nadic anhydride (6.9 ml, 0.048 mole) in DMF (50 ml) was refluxed with stirring under nitrogen for 4 hours. After cooling, it was poured into cold water (500 ml) with stirring, the precipitate filtered off, washed repeatedly with water and dried *in vacuo* at 40 °C to constant weight. It was purified by dissolving in chloroform and precipitated into ethanol. Its properties were the same as those of the material prepared without solvent.

(c) In xylene solvent

A mixture of CBH-103 (5.35g, 0.01 mole) and methyl nadic anhydride (3.45 ml, 0.024 mole) in xylene (50 ml) was refluxed in a flask fitted with a Dean Stark trap until the theoretical amount of water had been evolved and then cooled and the product filtered off and dried *in vacuo* at 40 °C to constant weight.

Its properties were the same as those of the material prepared without solvent.

Examples 3 to 10

Other bisnadimides prepared by methods similar to those described in Examples 1 and 2 are shown in Table 1. Their infrared and nuclear magnetic resonance spectra and their gel permeation chromatographs were in agreement with the proposed structures.

Table 1: Other Bisnadimides of Formula (II)

Example Number	X	Ar	Ar'
3	H	$(C_6H_3OC_6H_4)_2C(CH_3)_2$	1,4 disubstituted phenyl
4	H	$(C_6H_3OC_6H_4)_2C(CH_3)_2$	1,3 disubstituted methyl diethylphenyl
5	H	$C_6H_3CH_2C_6H_3$	1,4 disubstituted phenyl
6	CH_3	$(C_6H_3OC_6H_4)_2C(CH_3)_2$	1,4 disubstituted phenyl
7	CH_3	$(C_6H_3OC_6H_4)_2C(CH_3)_2$	1,3 disubstituted methyl diethylphenyl
8	CH_3	$C_6H_3COC_6H_3$	1,3 disubstituted methyl diethylphenyl
9	CH_3	$C_6H_3CH_2C_6H_3$	1,4 disubstituted phenyl
10	CH_3	$C_6H_3C(CH_3)_2C_6H_3$	1,4 disubstituted phenyl

Example 11

A matrix resin formulation was prepared for coating carbon fibre by dissolving 78% of the resin of Example 1, 18.0% trans-stilbene and 4% hydroquine in four volumes of dichloromethane with stirring. After coating with this solution to give a 40% total resin content on the fibres after drying, the cloth was laid up in a 5 layer test part and cured in a heated press as follows. 25 °C to 250 °C in 3 hrs, 250 - 310 °C

in 1 hr, 310 °C for 1 hr and then cooled to room temperature over 2 hrs. Measurements by DMTA indicated a T_g of 386 °C.

Example 12

A 20% (w/v) solution of the bisnadimide of Example 6 in methylene chloride was coated on to a carbon fibre cloth to give approximately a 40% resin content on the fibres after drying, the cloth was laid up in a 5 layer test part and cured in a heated press from 25 °C to 180 °C in 0.5 h, 180 °C/1 h, 200 °C/1.5 h, 250 °C/6 h and 315 °C/2 h.

Examples 13 to 18

Other bisnadimides were applied to carbon fibre cloth and cured by methods similar to those of Example 12. Some of the properties of the cured laminates are listed in Table 2. The value of the T_g for most of the examples can be increased by up to 50% by a post cure at 315 °C for several hours.

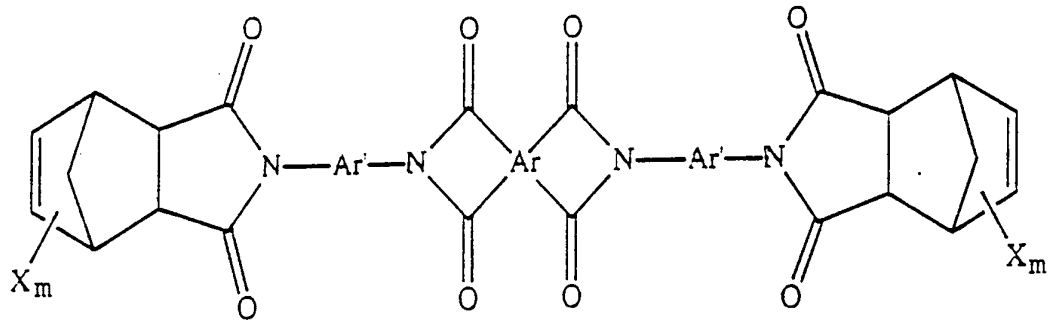
Table 2: Preparation and properties of some cured bisnadimide 5-ply carbon fibre laminates

Example	Bisnadimide of Example Number	Prepregging Solvent	Maximum Cure (°C)	Wt% Resin	Thickness of laminate (mm)	T_g by DMTA (°C)	Water uptake at 71°C after 7 days (%)	Weight Loss at 250°C after 7 days (%)
12	6	CH_2Cl_2	315	42	1.18	263	0.9	0.37
13	6	DMF	315	30	1.07	294	2.7	0.8
14	6	NMP	315	30	1.10	295	4.1	1.2
15	3	DMF	315	35	1.05	325	3.7	0.6
16	4	CH_2Cl_2	315	42	1.13	312	1.4	2.3
17	7	CH_2Cl_2	315	42	1.09	286	1.4	2.4
18	9	CH_2Cl_2	315	42	1.18	374	1.7	0.31

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

CLAIMS

1. A method for the preparation of a bisnadimide of Formula (II) substantially free of oligomeric, amidic and uncyclized impurities



Formula (II)

wherein

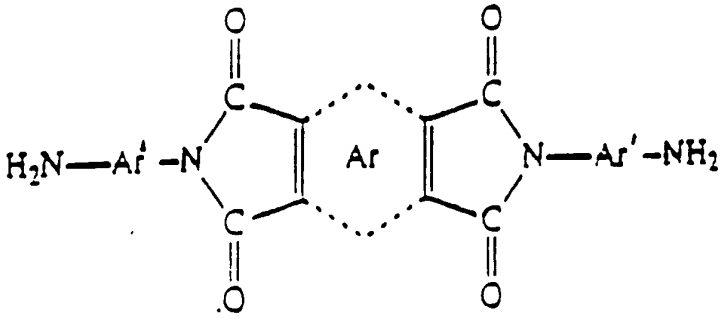
Ar is an optionally substituted aryl, optionally substituted bridged or bonded di- or poly- aryl or optionally substituted heteroaryl group,

Ar' is an optionally substituted aryl or heteroaryl group which provides for good conjugation between the nitrogen containing groups;

X is hydrogen, halogen or an alkyl group; and

m is 0 to 6

which comprises reacting a diaminobisimide of the Formula (III)



Formula (III)

wherein Ar and Ar' are as defined in Formula (II) above with nadic acid or a reactive derivative thereof which is optionally substituted with an alkyl group.

2. A method according to Claim 1, wherein the nadic acid derivative is nadic anhydride or an alkyl ester of nadic acid.

3. A method according to Claim 1 or Claim 2, wherein the reaction is performed at an elevated temperature.

4. A method according to Claim 3, wherein the temperature is above about 120 °C.

5. A method according to any one of the preceding claims, wherein the reaction is performed in the presence of a solvent.

6. A method according to Claim 5, wherein the solvent is an organic solvent.

7. A method according to Claim 5 or Claim 6, wherein the solvent is dimethylformamide, dimethylacetamide or xylene.

8. A bisnadimide of Formula (II) as defined in Claim 1 whenever prepared by the method of any one of the preceding claims.

9. A bisnadimide of Formula (II) as defined in Claim 1.

10. A curable formulation which comprises a bisnadimide of the Formula (II) as defined in Claim 8 or Claim 9.

11. A crosslinked polyimide polymer which is formed from a bisnadimide monomer of Formula (II) as defined in Claim 8 or Claim 9.

12. A method for the preparation of a crosslinked polyimide polymer as defined in Claim 11 which comprises heating a bisnadimide of Formula (II) as defined in Claim 8 or Claim 9.

13. A method according to Claim 13, wherein the heating occurs in the presence of a curing additive.

14. A method according to Claim 13, wherein the curing additive is trans-stilbene and/or hydroquinone.

15. An adhesive, bar, film or moulded component which is composed wholly or partly of the crosslinked polyimide polymer defined in Claim 11.

16. An impregnated fibre reinforced material wherein the fibre reinforcements are coated with the curable formulation defined in Claim 10.

17. An advanced composite material which comprises an assembly of reinforcing fibres in a matrix of the crosslinked polyimide polymer defined in Claim 11.

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[5] C07D 487/04, 403/14, C08G 73/10, C09J 179/08, D06M 15/59

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C07D 487/04, 403/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

DERWENT: PHTHALIMIDO: and ISOINDOL:
JAPIO: PHTHALIMIDO: and ISOINDOL:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	AU,A,86280/91 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 16 April 1992 (16.04.92) page 21 line 9 to page 24 line 24	1-9
A	AU,B,50572/72 (462823) (FUJI PHOTO FILM CO. LTD.) 4 July 1974 (04.07.74) page 44 line 1	1-9
A	AU,B,28625/57 (220290) (E.I. DU PONT DE NEMOURS AND COMPANY) 19 December 1957 (19.12.57) column 2 lines 13-25	1-9

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 1994 (10.02.94)	02. 03. 94

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	**Citation of document, with indication, where appropriate of the relevant passages**	**Relevant to Claim No.**
A	US,A,3998786 (UNIVERSITY OF NOTRE DAME DU LAC) 21 December 1976 (21.12.76) column 3 lines 43-54	1-9

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	86280/91	NZ	240089	WO	92/06078		
AU	50572/72	BE	793446	BR	7209220	CA	1041343
		CH	561436	DE	2263875	FR	2169879
		GB	1421123	GB	1421126	IT	974398
		JP	48073147	NL	7217721	US	4269936
US	3998786	DE	2425163	FR	2230675	JP	50022091
		NL	7407022	US	4055543	US	4075171
		DE	2425164	FR	2230676	JP	50027883
		NL	7407023	US	3897395	US	4026833
		US	4026871	US	4058505	US	4060515
		US	4197397	US	4537947		

END OF ANNEX