COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

6 0 0 3 9

APPLICATION FOR A STANDARD PATENT

I/We RHONE-POULENC CHIMIE, of 25, quai Paul Doumer, 92408 Courbevoie, France

hereby apply for the grant of a Standard Patent for an invention entitled:

"POLYMERS BASED ON BORON AND NITROGEN, THEIR PREPARATION AND THEIR USE"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application~~(s)~~:—

Number	Convention Country	Date
87/12586	France	11th September, 1987

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 1.3.91

M002711 09/09/88

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 9th day of September, 1988.

To: THE COMMISSIONER OF PATENTS

.....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

~~K3714~~

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention

Insert title of invention.

entitled: POLYMERS BASED ON BORON AND NITROGEN, THEIR PREPARATION AND THEIR USE

Insert full name(s) and address(es) of Declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I / ~~We~~ Madeleine France Fabre

of: RHONE-POULENC CHIMIE, a French Body Corporate,

of: 25, quai Paul Doumer, 92408 COURBEVOIE, France.

do solemnly and sincerely declare as follows :-

Cross out whichever of paragraphs 1(a) or 1(b) does not apply.

1(a) relates to application made by individual(s).

1(b) relates to application made by company; insert name of applicant company.

~~1(a) I am / We are the applicant for the patent~~

or (b) I am authorized by

RHONE-POULENC CHIMIE,

the applicant.S..... for the patent to make this declaration on ~~its~~ / their behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply.

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

~~2(a) I am / We are the actual inventor of the invention~~

or (b)

GERARD MIGNANI and JEAN-JACQUES LEBRUN, Both citizens of France of: 2, avenue des Freres Lumiere, 69008 - LYON, France and 24, rue Pierre Brunier, 69300 - CALUIRE, France respectively.

~~I~~ / ~~We~~ are the actual inventor..S..... of the invention and the facts upon which the applicant.S..... ~~is~~ / ~~are~~ entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

"The applicant would, if a patent were granted upon an application made by the Inventors, be entitled to have the patent assigned to it"

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was / were~~ made

in FRANCE NO. 87/12586 ..... on the 11 SEPTEMBER, 1987

by RHONE-POULENC CHIMIE .....

in ..... on the .....

by .....

in ..... on the .....

by .....

4 The basic application..... referred to in paragraph 3 of this Declaration ~~was / were~~ the first application..... made in a Convention country in respect of the invention the subject of the application

Insert place and date of signature.

Declared at COURBEVOIE this 21st day of September 1988

Signature of Declarant(s) (no attestation required).

M-F Fabre

Madeleine France FABRE

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-22097/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 610239

(54) Title
POLYMERS BASED ON BORON AND NITROGEN, THEIR PREPARATION AND THEIR USE

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(74) Attorney or Agent
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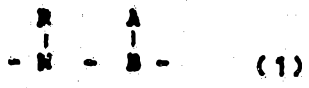
(56) Prior Art Documents
AU 22096/88 C08G 79/08
US 4581468
GB 2163761

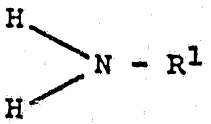
(57) Claim

1. Process for preparing a polymer based on boron and nitrogen, which comprises reacting (a) a mixture comprising a trihaloborane (compound A) and a cyclic compound (compound B) consisting of repeated units of formula:



(1)

in which A denotes a halogen atom and R denotes a hydrogen atom, a hydrocarbon radical, or an organosilyl or hydrogenoorgano-silyl radical, with (b) a compound comprising at least one NH_2 group and of the formula



(2)

.../2

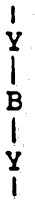
in which the radical R^1 is hydrogen, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical (compound C).

16. Polymer based on boron and nitrogen, having per molecule:

(a) at least one unit of formula:

(I)

and (b) at least one unit of formula:



(II)

in which formulae X denotes $N-R^1$ and Y denotes N-R, and the radicals R and R^1, which may be identical or different, are each a hydrogen atom, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

610239

(Original)

FOR OFFICE USE

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant: RHONE-POULENC CHIMIE

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France

Actual Inventor(s): Gerard Mignani and
Jean-Jacques Lebrun

Address for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete specification for the invention entitled:

"POLYMERS BASED ON BORON AND NITROGEN, THEIR PREPARATION AND THEIR USE"

The following statement is a full description of this invention, including the best method of performing it known to us :-

The present invention relates to polymers based on boron and nitrogen, their preparation and their use, especially in the manufacture of ceramic articles and products based on boron nitride, in particular in the form of fibres.

Boron nitride is in increasing demand, because, in particular, of its stability at high temperatures, its resistance to thermal shocks, its great chemical inertness and its very good thermal conductivity. Moreover, its low electrical conductivity makes it an insulating material of choice.

Various processes are known for preparing boron nitride. One such process consists in reacting boron trichloride with ammonia in the gaseous phase. A fine powder of boron nitride is thereby obtained, which it is possible to sinter in order to produce items having bulk. However, the items obtained possess a microporosity which can be very troublesome for certain applications.

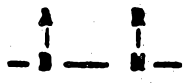
More recently, it has been discovered that it is possible to prepare boron nitride by the pyrolysis of precursor polymers.

The advantage of the polymer method resides, above all, in the possibility of shaping this type of product, and more especially for the production, after pyrolysis, of boron nitride fibres. Thus, in US Patent 4,581,468, an organoboron polymer has been described which is obtained by the action of ammonia (ammonolysis) on a trichloro-(trialkylsilyl)borazole (cyclic compound), and which, it is stated, enables boron nitride fibres to be obtained after spinning followed by pyrolysis at 970°C. However, the cyclic polymer described in this document is very difficult to prepare, and hence expensive, and as a result can scarcely hold out the hope of application on the scale of an industrial production. Furthermore, the maximum weight yield of boron nitride capable of being obtained with this type of product does not exceed 22%, which implies, self-evidently, actual yields that are much lower than this value.

The present invention reduces or solves the above problems and proposes economical, effective and simple means that are easy to carry out for obtaining, in the most diverse forms (threads, fibres, moulded articles, coatings, thin layers, films, and the like), organometallic polymers based on boron and nitrogen which, on pyrolysis, give products based on boron nitride in a high weight yield.

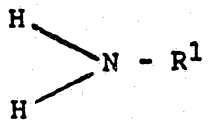
It has now been found that boron nitride can be

obtained in high weight yields from precursor polymers based on boron and nitrogen when these polymers have been prepared by a process which comprises reacting (a) a mixture comprising a trihaloborane (compound A) and a cyclic compound (compound B) consisting of repeated units of formula:



(1)

in which A denotes a halogen atom and R denotes hydrogen, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical, with (b) a compound comprising at least one NH_2 group and of the formula



(2)

in which the radical R^1 is hydrogen, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical (compound C).

For the remainder of the description, the compounds C are referred to as aminolysis agents in the most general case (amino compound possessing at least one NH_2 group), and an ammonolysis agent in the more special case where it is ammonia. Furthermore, and in consequence of the foregoing, the reaction products obtained from the compounds A, B and C are referred to, according to the case, as aminolysates or ammonolysates, the latter hence being included in the family of aminolysates.

Three aminolysates, as will be explained in greater detail below, are new polymers based on boron and nitrogen that constitute a second subject of the present invention.

The process of the invention is hence based

essentially on a co-aminolysis of a mixture of at least one trihaloborane and at least one cyclic compound B as defined above.

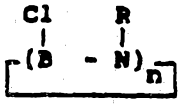
The Applicant has discovered that, altogether unexpectedly and surprisingly, this coaminolysis enables polymers to be obtained to which an especially cross-linked network structure imparts an increased thermal stability on pyrolysis, and thereby increases the yields of boron nitride.

Furthermore, and this is an additional advantage of the process according to the invention over the processes of the prior art (US Patent 4,581,468), the fact that the new process is operated with mixtures based on trihaloborane, which is a compound that is easy to prepare industrially and hence inexpensive, makes it possible to reduce substantially the quantity of cyclic compounds to be used, which makes the process of the invention especially economical.

The starting compound A generally used is trichloroborane, although any other haloborane may be suitable, such as, for example, a trifluoro-, a tribromo- or a triiodoborane.

The starting cyclic compound B is also generally a chlorinated compound.

This compound preferably corresponds to the following formula:



in which the radical R, as already stated, denotes a hydrogen atom, a hydrocarbon radical or an organosilyl or hydrogenoorganosilyl radical, and the subscript n denotes an integer between 2 and 20, and preferably between 3 and 10.

The most commonly used hydrocarbon radicals are alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl radicals, as well as alkenyl and alkynyl radicals.

Among alkyl radicals suitable for the present invention, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl radicals may be mentioned by way of examples. Among cycloalkyl radicals, cyclopentyl, cyclohexyl and cycloheptyl radicals may be mentioned. By way of aryl radicals: phenyl and naphthyl radicals; alkylaryl radicals: tolyl and xylyl radicals; and finally arylalkyl radicals: benzyl and phenylethyl radicals.

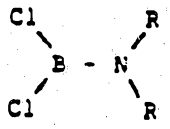
By way of alkenyl radicals, vinyl, allyl, butenyl and pentenyl radicals may be mentioned more especially.

Finally, ethynyl, propynyl and butynyl radicals may be mentioned as alkynyl radicals.

According to a preferred embodiment of the

invention, the radical R is an organosilyl radical, and more especially a (triorgano)silyl radical. Still more preferably, R is a (trialkyl)silyl radical, such as, in particular, a trimethyl-, triethyl-, tripropyl-, tributyl-, tripentyl-, trihexyl-, triheptyl- and trioctylsilyl radical. The (trimethyl)silyl radical is especially suitable.

The cyclic compounds B defined above are well known, and may be prepared by any means known per se. Corresponding compounds of the type



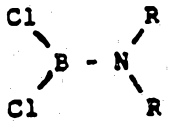
(R having the meaning given above) may, in particular, be prepared by thermolysis, in xylene under reflux or in the vapour phase, and according to procedures such as are already described in the literature [see, for example, R.L. WELLS in Inorg. Chemistry, 2, (1963), 29, as well as P. GEYMAYER in Monatsh, 97, (1966), 429].

These latter compounds are also well known to those skilled in the art.

For example, when R is alkyl, reference may be made, in particular, to the work of WILBERG and SCHUSTER (Zeitschrift für Anorganische Chemie, 1933,213, page 77), of BROWN (Journal of American Chemical Society, 1952, 74, page 1219), or alternatively of BURG and BANUS (Journal of American Chemical Society, 1954, 76, page 3903).

When R is a triorganosilyl radical, reference may be made to the work of JENNE and NIEDENZU (Inorganic Chemistry, 1964, 3, 68), of SUJISHII and WITZ (Journal of American Ceramic Society, 1957, 79, page 2447), or alternatively of WANNAGAT (Angew Chemie International Edition, 3, 1964, page 633).

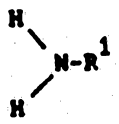
Generally speaking, the desired compound of formula



may be obtained by the action of BCl_3 on  , under suitable conditions of temperature and mole ratio.

Finally, as regards the aminolysis agents (compound C) participating in the process of the invention, ammonia, primary amines, diamines (hydrazine, alkylhydrazine, hydrazide, alkylenediamine, etc.), amides, silylamines and the like, may be mentioned.

~~However,~~ Compounds which correspond to the following formula (2)



(2)

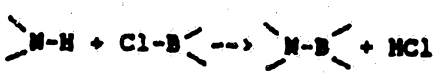
in which the radical R^1 is hydrogen,

a hydrocarbon radical or a silyl radical, are ~~preferably~~ used. ~~Thus,~~ The following are more especially suitable:

- ammonia (R^1 = hydrogen)
- primary organoamines (R^1 = alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radical, such as, for example, methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine and octylamine, cyclopropylamine, phenylamine, etc.
- silylamines, and more especially triorganosilylamines such as (trimethylsilyl)amine and (triethylsilyl)amine, or alternatively hydrogenoorganosilylamines such as (hydrogenodimethylsilyl)amine.

Primary alkylamines and especially ammonia are the preferred aminolysis agents.

The general scheme for the aminolysis reactions in the reaction medium is as follows:



The aminolysis reaction may be performed in bulk, or, preferably, in an organic solvent medium (hexane, pentane, toluene, etc.) and under anhydrous conditions.

It is generally performed at atmospheric pressure, although lower or higher pressures are clearly not ruled

out.

Furthermore, since aminolysis reactions are generally fairly exothermic, it is preferable to work at low temperature.

The reaction time, depending on the quantities of reactants introduced, can vary from a few minutes to several hours.

The mole ratio in the starting mixture between the trihaloborane and the cyclic compound can vary very widely. Generally speaking, it is observed that, the greater the percentage of trihaloborane in this mixture, the higher the pyrolytic yield of boron nitride obtained from the polymer at the end of the reaction. According to a preferred embodiment of the invention, the mole ratio compound A/compound B in the starting mixture is at least 1.

At the end of this reaction stage, the polymer is separated from the reaction medium, in particular from the ammonium chloride formed, this being done by any means known per se, for example by filtration, or alternatively by extraction and separation after settling has occurred, by means, in particular, of an ammonia solution.

The polymer thus recovered, optionally after the removal of the solvent followed by drying, then constitutes the product.

Apart from the general preparation process described above, the invention also provides, as new

products, polymers based on boron and nitrogen, capable of being obtained, in particular, by the said process, and which show, on pyrolysis, especially high weight yields of boron nitride.

It has now been found that boron nitride may be obtained in high weight yields from a precursor polymer based on boron and nitrogen, the said polymer being characterized in that it possesses per molecule:

(a) at least one unit of formula (I):

(I)

and (b) at least one unit of formula (II):

(II)

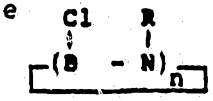
in which formulae X denotes $N-R^1$ and Y denotes N-R, the radicals R and R^1, which may be identical or different, each being hydrogen, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical.

The Applicant has, in effect, discovered that such polymers based on boron and nitrogen, which possess a network structure essentially composed of a combination of units of (I) and units of formula (II) as defined above, show a behaviour on pyrolysis which is markedly improved in comparison with the precursors known hitherto, and thereby also enable materials based on boron nitride

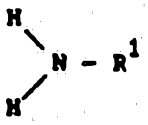
to be obtained with good weight yields of ceramic.

It will already have been understood that it is possible to obtain polymers possessing all the desired units (I) and (II), that is to say all the desired radicals R and R^1, simply by reacting compounds B and C as defined above which possess the same radicals R and R^1.

More specifically, and without it being desired to limit the present invention to the theory, if the starting mixture comprises BCl_3 (compound A) and a cyclic compound of the type

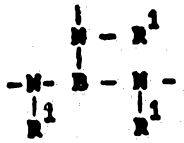


(compound B), the co-aminolysis of this mixture with a compound of the type



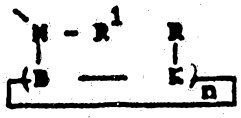
(compound C)

will lead, according to known mechanisms, to a polymer essentially composed of a combination, of the random type, between units of formula (I):



(I)

and units of the formula (III):



(III)

the latter, of course, themselves being only a formal

repetition of n units of formula (II) as defined above.

Similarly, the ratio between the units of formula (I) and those of formula (II) in the final polymer may be adjusted simply by means of the appropriate ratio between the compounds A and the compounds B initially present in the reaction medium.

According to a preferred embodiment of the invention, the polymer contains at least 50 mol % of units of formula (I).

Generally speaking, it is observed that, the higher percentage of units (I), the greater the yield of boron nitride after pyrolysis.

By way of hydrocarbon and silyl radicals suitable for the polymers according to the invention, reference may be made to the various examples already given for the radicals R and R^1 of the compounds B and C.

Alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl radicals, as well as (triorgano)silyl radicals such as, for example, (trialkyl)silyl radicals, are thus more especially suitable.

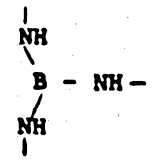
According to a preferred embodiment of the invention, the radical R^1 is chosen from the hydrogen atom and alkyl radicals.

Still more preferably, the radical R^1 denotes a hydrogen atom.

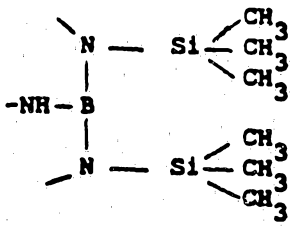
Furthermore, to obtain the best yields of ceramic on pyrolysis, it is preferable to choose the radical R from

organosilyl radicals, and more especially from (trialkyl)-silyl radicals.

In an especially preferred example of a polymer according to the invention, the units (I) and (II) are of the following type:



(I)



(II)

The polymers according to the invention possess a number average molar mass which can be between 300 and 50,000, and preferably between 500 and 5,000.

Furthermore, they possess a weight average molar mass which can extend between 600 and 100,000, and preferably between 1,000 and 10,000.

Depending on the mole ratio existing between the units of formula (I) and of formula (II), the polymers according to the invention can, at room temperature, occur in a form ranging from a fairly viscous or very viscous oil to the solid state. Generally speaking, a high content of units of formula (I) corresponds to a polymer of high molecular weight, and hence of high viscosity.

The polymers according to the invention are,

furthermore, soluble in most of the usual organic solvents (hexane, toluene, etc.), which can be very advantageous in respect of their potential for being shaped.

The polymers based on boron and nitrogen according to the invention find a very special application in the manufacture of ceramic articles and products containing, at least partially, boron nitride.

In the most general case (production of powders), the polymer is then pyrolysed in an inert atmosphere, under vacuum or, preferably, under ammonia, at a temperature ranging from 100 to 2,000°C, until the polymer is converted completely to boron nitride.

The polymer, before pyrolysis, can also be shaped, by moulding or by spinning, for example. In the case where it is desired to obtain fibres, the polymer is spun by means of a conventional die (after melting, where appropriate, if the polymer is initially in the solid state), and is then treated thermally at a temperature ranging from 100 to 2,000°C, and preferably under an ammonium atmosphere, to give a boron nitride fibre.

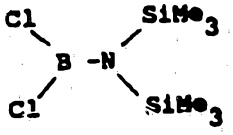
The fibres obtained may then be used as a reinforcing structure for composite materials of the ceramic/ceramic or ceramic/metal type.

The following Examples illustrate the invention.

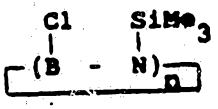
Example 1

80 ml of dry hexane, 3.4 g (0.029 mol) of BCl_3

and 2.8 g (0.007 mol) of a compound prepared by the thermolysis in xylene under reflux and according to the method described in the literature [R.L. WELLS: Inorg. Chemistry, 2 (1963), 28 and P. GEYMAYER: Monatsch, 97 (1966), 429] of:



the said compound obtained corresponding essentially to the formula:



with n predominantly equal to 3, are introduced at -5°C and under nitrogen into a 250-ml round-bottomed flask.

Ammonia is then introduced into this mixture for 1 hour at a flow rate of 7.5 litres/hour. A white precipitate then forms, composed predominantly of ammonium chloride.

After filtration and evaporation of the solvent, 2.35 g of a very viscous oil, constituting the polymer according to the invention, are recovered.

The yield of product isolated from the co-ammonolysis reaction is 70%.

The characteristics of the polymer are as follows:

Mn = 1,000 (number average molar mass)

Mw = 2,000 (weight average molar mass)

PI = 1.97 (polydispersity index)

TGA (under argon at 950°C): 19.9%.

The pyrolysis of this polymer under nitrogen leads to a white ceramic which essentially contains boron nitride.

The weight yield of the pyrolysis at 1,100°C is 25.4%; it becomes 21.4% at 1,500°C.

Example 2

10.2 g (0.0870 mol) of BCl_3, 8.05 g (0.0201 mol) of $\left[\begin{matrix}Cl\\|\\(B-N)\end{matrix}\right]_n$ $\begin{matrix}SiMe_3\\|\end{matrix}$, with n predominantly equal to 3 (prepared as in Example 1) and 250 ml of dry hexane are introduced under nitrogen into a 500-ml three-necked flask.

This mixture is cooled to -46°C; gaseous ammonia (5.82 mol) are introduced therein; the reaction is then exothermic and the temperature of the mixture is maintained at about -15°C to -18°C during the introduction of ammonia (reaction time: 3 h).

After filtration under nitrogen, there are recovered 21.3 g of a white solid predominantly containing ammonium chloride, and a hexane solution which is then evaporated; 5.4 g of a white solid, constituting the polymer according to the invention, are then recovered.

The yield of product isolated from the co-ammonolysis reaction is 53%.

The characteristics of the polymer are as follows:

$\overline{Mn}$ = 1,580

$\overline{Mw}$ = 4,680

PI = 2.93

Ps = 150°C (softening point)

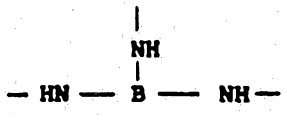
TGA (argon: 800°C): 30.28%.

The pyrolysis of this polymer under nitrogen leads to a white ceramic, which essentially contains boron nitride.

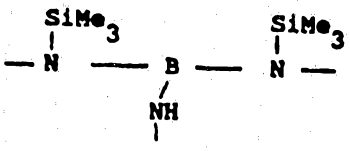
The yield of the pyrolysis at 1,100°C is 30.1%.

These results clearly demonstrate the advantage of the process according to the invention for obtaining polymers based on boron and nitrogen, on the one hand having high molecular weights, and on the other hand having improved thermal behaviour, and accordingly showing markedly increased yields of boron nitride on pyrolysis.

For both experiments, analysis shows that the polymers obtained consist essentially of a combination of units of formula:

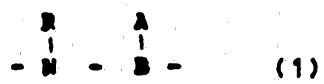


and units of formula:



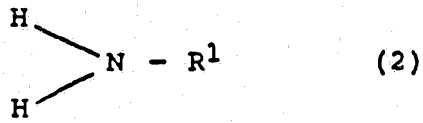
The claims defining the invention are as follows:

1. Process for preparing a polymer based on boron and nitrogen, which comprises reacting (a) a mixture comprising a trihaloborane (compound A) and a cyclic compound (compound B) consisting of repeated units of formula:



(1)

in which A denotes a halogen atom and R denotes a hydrogen atom, a hydrocarbon radical, or an organosilyl or hydrogenoorgano-silyl radical, with (b) a compound comprising at least one NH_2 group and of the formula



(2)

in which the radical R^1 is hydrogen, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical (compound C).

2. Process according to Claim 1, in which the reaction is performed in bulk.

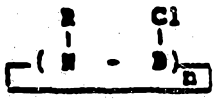
3. Process according to Claim 1, in which the reaction is performed in solution in an anhydrous organic solvent.

4. Process according to any one of the preceding claims, in which the mole ratio of compound A to compound B in the said mixture is at least equal to 1.

5. Process according to any one of the preceding claims, in which the trihaloborane (compound A) is trichloroborane.

6. Process according to any one of the preceding claims, in which A denotes chlorine.

7. Process according to Claim 6 in which the compound B corresponds to the formula:



in which the subscript n is an integer from 2 to 20.

8. Process according to Claim 7, in which the subscript n is from 3 to 10.

9. Process according to any one of the preceding claims, in which the hydrocarbon radical R is alkyl, cycloalkyl, aryl, alkylaryl, arylalkyl, alkenyl or alkynyl.

10. Process according to any one of claims 1 to 8, in which the radical R is an organosilyl radical.

11. Process according to Claim 10, in which the radical R is a (triorgano)silyl radical.

12. Process according to Claim 11, in which the radical R is a (trialkyl)silyl radical.

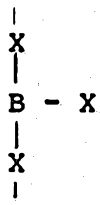
13. Process according to any one of the preceding claims, in which the radical R^1 is hydrogen or alkyl.

14. Process according to Claim 1 substantially as described in Example 1 or 2.

15. Polymer based on boron and nitrogen, obtained by a process as defined in any one of claims 1 to 14.

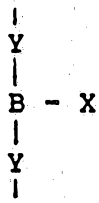
16. Polymer based on boron and nitrogen, having per molecule:

(a) at least one unit of formula:



(I)

and (b) at least one unit of formula:



(II)

in which formulae X denotes $N-R^1$ and Y denotes N-R, and the radicals R and R^1, which may be identical or different, are each a hydrogen atom, a hydrocarbon radical, or an organosilyl or hydrogenoorganosilyl radical.

17. Polymer according to claim 16, in which the mole ratio between the units of formula (I) and the units of formula (II) is at least equal to 1.

18. Polymer according to Claim 16 or 17, in which the radical R is alkyl, cycloalkyl, aryl, arylalkyl, alkylaryl, alkenyl or alkynyl.

19. Polymer according to Claim 16 or 17, in which the radical R is an organosilyl radical.

20. Polymer according to Claim 19, in which the radical R is a (triorgano)silyl radical.

21. Polymer according to Claim 20, in which the radical R is a (trialkyl)silyl radical.

22. Polymer according to any one of claims 16 to 21, in which the radical R^1 is hydrogen or alkyl.

23. Polymer according to any one of claims 16 to 22, having a number average molar mass between 300 and 50,000.

24. Polymer according to Claim 23 having a number average molecular mass between 500 and 5,000.

25. Polymer according to any one of claims 16 to 24, having a weight average molar mass of between 600 and 100,000.

26. Polymer according to Claim 25 having a weight average molar mass between 1,000 and 10,000.

27. Boron nitride fibre obtained by spinning a polymer as claimed in any one of claims 15 to 26 followed by pyrolysis at a temperature from 100 to 2,000°C in an inert atmosphere under vacuum.

28. Boron nitride fibre obtained by spinning a polymer as claimed in any of claims 15 to 26 followed by pyrolysis at a temperature of between 100 and 2000°C in an inert atmosphere under ammonia .

Dated this 7th day of February, 1991.

RHONE-POULENC CHIMIE
By Its Patent Attorneys
DAVIES & COLLISON