

Method of manufacturing conductive heterocyclic polymers, new heterocyclic conductive polymers, new intermediate products for the preparation of the polymers, and synthesis of the intermediate products

Citation for published version (APA):

Pouwer, K. L., Vries, T. R., Meijer, E. W., & Wynberg, H. (1989). Method of manufacturing conductive heterocyclic polymers, new heterocyclic conductive polymers, new intermediate products for the preparation of the polymers, and synthesis of the intermediate products.

Document status and date:

Published: 01/01/1989

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

EP0340826B1

Publication Title:

Method of manufacturing conductive heterocyclic polymers, new heterocyclic conductive polymers, new intermediate products for the preparation of the polymers, and synthesis of the intermediate products

Abstract:

The polymers are prepared by using the new intermediate product which forms a polymeric precursor, and which is converted into the desired heterocyclic polymer by ring closure.

Data supplied from the esp@cenet database - <http://ep.espacenet.com>

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 340 826 B1

12

EUROPEAN PATENT SPECIFICATION

- 45 Date of publication of patent specification: **02.02.94** 51 Int. Cl.⁵: **C08G 61/12, C08G 16/02, C08G 16/04, H01B 1/12**
- 21 Application number: **89200960.6**
- 22 Date of filing: **17.04.89**

- 54 **Method of manufacturing conductive heterocyclic polymers, new heterocyclic conductive polymers, new intermediate products for the preparation of the polymers, and synthesis of the intermediate products.**

- 30 Priority: **21.04.88 NL 8801031**

- 43 Date of publication of application:
08.11.89 Bulletin 89/45

- 45 Publication of the grant of the patent:
02.02.94 Bulletin 94/05

- 84 Designated Contracting States:
DE FR GB IT NL

- 56 References cited:
EP-A- 0 095 412 EP-A- 0 098 988
EP-A- 0 099 984 EP-A- 0 203 438
EP-A- 0 241 306 FR-A- 2 077 078
US-A- 4 521 589

MACROMOLECULAR CHEMISTRY; RAPID COMMUNICATIONS vol. 6, pages 679-684, 1985; J.P. MONTHEARD et al.: "dopage par l'iode et le pentafluorure d'arsenic de copolymères aromatiques et hétérocycliques. Comportement thermique de complexes copolymère-iodé" page 679, formula 1*

- 73 Proprietor: **N.V. Philips' Gloeilampenfabrieken Groenewoudseweg 1 NL-5621 BA Eindhoven(NL)**

- 72 Inventor: **Pouwer, Kornelis Lammert c/o INT. OCTROOIBUREAU B.V. Prof. Holstlaan 6 NL-5656 AA Eindhoven(NL)**
 Inventor: **Vries, Ton René c/o INT. OCTROOIBUREAU B.V. Prof. Holstlaan 6 NL-5656 AA Eindhoven(NL)**
 Inventor: **Meijer, Egbert Willem c/o INT. OCTROOIBUREAU B.V. Prof. Holstlaan 6 NL-5656 AA Eindhoven(NL)**
 Inventor: **Havinga, Edsko Enno c/o INT. OCTROOIBUREAU B.V. Prof. Holstlaan 6 NL-5656 AA Eindhoven(NL)**
 Inventor: **Wijnberg, Hans c/o INT. OCTROOIBUREAU B.V. Prof. Holstlaan 6 NL-5656 AA Eindhoven(NL)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 340 826 B1

EP 0 340 826 B1

⑦ Representative: **Weening, Cornelis et al**
INTERNATIONAAL OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)

Description

The invention relates to a method of preparing electrically conductive heterocyclic polymers comprising a thiophene ring or a pyrrole ring.

5 Polypyrrole, polythiophene and polyphenylenethiophene are well-known, electrically conductive heterocyclic polymers. The electrically conductive character can be attained by treating (doping) the customarily manufactured polypyrrole, polythiophene or polyphenylenethiophene with J_2 , mostly in the gas phase at for example 100°C , or with AsF_5 . As a result hereof, electrons are extracted from the polymer which, hence, forms a polymer cation, the J_3^- ion or the AsF_6^- ion, which is also formed in this process, being
10 the counterion which is bonded to the polymer cation.

The well-known methods of preparing polypyrrole, polythiophene and polyphenylenethiophene are all based on the coupling of monomers in which the thiophene ring, the pyrrole ring and the phenyl ring is already present.

For example, polyphenylenethiophene is manufactured by subjecting 2,5-dibromothiophene and 1,4-dibromobenzene to Grignard coupling as is known from, for example, Die Macromol. Chemie, Rapid Commun. 6, p. 679 (1985). Polythiophene can alternatively be manufactured by subjecting 2,5-dibromothiophene Grignard coupling, as described in Synthetic Metals 9, p. 77 (1984). Polythiophene and polypyrrole are mostly prepared by electrochemical oxidation, in which at the anode the monomer molecules are converted by oxidation into the corresponding cations which are coupled to each other. By
20 means of chemical oxidation using, for example, FeCl_3 it is alternatively possible to convert the molecules of the monomer, such as pyrrole molecules, into cations which are subsequently coupled to form the polypyrrole molecules. The polymer formed in these oxidation processes already has a conductive character.

The well-known methods have the disadvantage that at a relatively limited chain length of, for example,
25 approximately 20 monomer units the products formed can no longer be dissolved in the reaction medium and, consequently, are separated, so that further polymerization into longer chains is prevented. Consequently, the length of the conjugated system present in the molecule is relatively short so that the electric conductivity is not optimal. In addition, the conjugated system must not be interrupted by faults sometimes occurring in the electrochemical method.

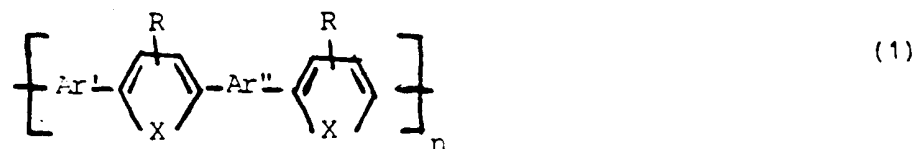
30 It is an object of the invention to provide a new method of manufacturing electrically conductive heterocyclic polymers, by means of which longer molecular chains and hence an improved electric conductivity can be obtained.

A further object of the invention is to provide a method which is suitable for general use and by means of which a wide composition range of heterocyclic polymers comprising a thiophene or pyrrole ring can be
35 manufactured.

According to the invention, these objects are achieved by means of a method which is essentially characterized by the application of a polymeric precursor comprising keto groups, which is converted into the desired heterocyclic thiophene polymer or pyrrole polymer by ring closure, which polymer is subsequently rendered electrically conductive in a customary manner by means of doping. Thus, the formation of
40 the heterocyclic ring takes place in the polymeric phase, which is in contrast with the methods known so far, in which, as described hereinbefore, the monomer used already comprises the intended heterocyclic ring.

The invention relates more particularly to a method of the type described above, which is characterized in that polymers are manufactured with correspond to the formula

45



50

wherein Ar' and Ar'' both represent an aromatic group, which aromatic groups are the same or different,

R is a hydrogen atom or an alkyl group having 1-10 C-atoms,

55 X is a sulphur atom or the group -NH-

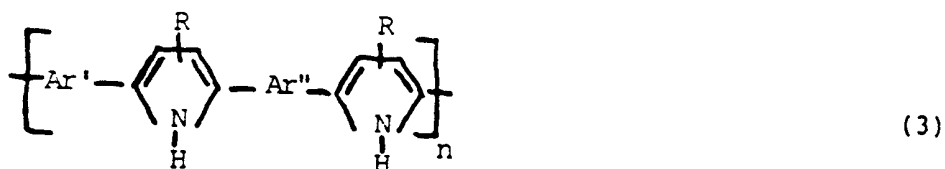
n is larger than or equal to 25,

by reacting a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning, with

a) NH₃ or a NH₃-producing substance, to obtain a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning, or

b) a sulphur-phosphor compound, to obtain a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning.

This method can be explained as follows.

ad. a:

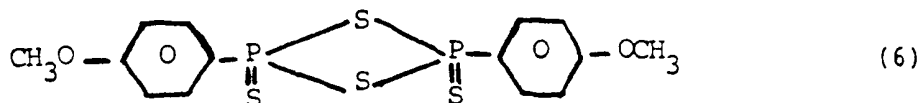
The reaction is preferably carried out using NH₃ gas at a raised temperature of, for example, 150-250 °C. The best results are obtained at 250 °C. It is also possible to apply an increased pressure. For this purpose, a reaction vessel comprising the compound of formula (2) is accommodated in an autoclave and NH₃ is introduced at a pressure of, for example, 5-20 bar.

The reaction indicated under a can also be carried out using an NH₃ producing substance such as an ammonium salt.

Preferably, liquid ammonium acetate is used or a solution of ammonium acetate in an inert organic solvent such as dimethyl formamide (DMF). The reaction in which liquid ammonium acetate is used is carried out in an inert gas atmosphere of, for example, N₂ at a raised temperature of, for example, 125 °C. The reaction in which the solution of ammonium acetate is used is also carried out in an inert gas atmosphere at the reflux temperature of the solvent used.

ad. b

The reaction indicated under b is preferably carried out at a raised temperature and in the presence of a solvent. Very suitable sulphur-phosphor compounds are P₂S₅ and Lawessons reagent. This reagent (LR) has the formula:



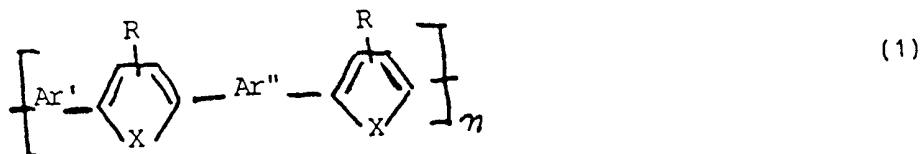
Suitable inert organic solvents are, for example, aliphatic and aromatic hydrocarbons which may be chlorinated and ethers. Preferably, the reaction temperature is 150-250 °C because at these relatively high temperatures the best degree of conversion is obtained. Preferably, the boiling temperature of the solvent is

as high as possible. A suitable solvent is, in particular, O-dichlorobenzene having a boiling point of 180° C.

In the above-stated formulae Ar' and Ar'' are an aromatic group. The choice of the aromatic group is not restricted within narrow limits. Examples of suitable aromatic groups are benzene, anthracene, pyridine, thiophene and pyrrole. These groups may be substituted by one or more halogen atoms, alkyl groups and aryl groups. The value of n is equal to or larger than 25. There is no clear maximum value of n. In general the value of n is smaller than 2500. A suitable value is 25 ≤ n ≤ 100.

New, electrically conductive polymers can be manufactured by using the method according to the invention.

The invention also relates to such new compounds which correspond to the formula



wherein Ar', Ar'', R, X and n have the above-stated meaning, and if X is a -NH-group and R is a H-atom, Ar' and Ar'' do not both represent a pyrrole group, and if X is a -S-atom and R is a H atom, Ar' and Ar'' do not both represent a thiophene group or a phenyl group, further excepting linear poly(3-alkyl-2,5-thienylene) polymers having a lower alkyl group and a degree of polymerization n = 25-100.

Suitable electrically conductive polymers are, in particular, the compounds of formula (1), wherein Ar' and Ar'' both have the same meaning and represent a phenyl group, a pyrrole group, a thiophene group or a pyridine group, and wherein R is a hydrogen atom, with the proviso that if Ar' and Ar'' both are a thiophene or a phenyl group, X is a -NH-group, and if Ar' and Ar'' both are a pyrrole group, X is a -S- atom.

A very interesting new compound is polyphenylenepyrrole, which comprises 25-100 monomer units per molecule.

The new compounds according to the invention can be prepared by means of the method mentioned hereinbefore. The intermediate product used in the method according to the invention is new. This intermediate product is important because by further conversions the interesting electrically conductive polymers can be manufactured from this product.

The invention also relates to the new intermediate product which corresponds to the formula



wherein Ar', Ar'', R and n have the above-stated meaning.

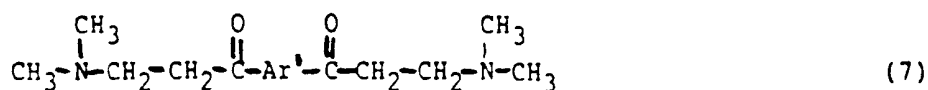
Interesting intermediate products are in particular the compounds of formula (2), wherein Ar' and Ar'' have the same meaning and represent a phenyl group, pyrrole group, thiophene group or a pyridene group, and R is a hydrogen atom.

The polymer compounds of formula (2) are manufactured according to a new polymerization method. This new polymerization process also forms part of the present invention.

The invention more particularly relates to a method of manufacturing a polymeric substance which corresponds to the formula



wherein Ar', Ar'', R and n have the above-stated meaning, and which is characterized in that a compound of the formula



5 is made to react with a compound of the formula



thereby forming a polymer of formula (2), wherein R is a hydrogen atom. If desired, this polymeric compound is alkylated into a compound of formula (2) wherein R is an alkyl group.

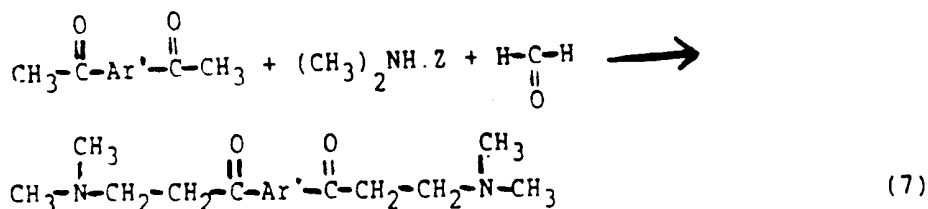
15 The above-stated reaction is carried out in a solvent such as dimethyl formamide and in the presence of a catalytic quantity of a cyanide, in particular NaCN. The alkylation process proceeds smoothly, for example, by making the compound to be alkylated react with a mixture of KOH, dimethyl sulphoxide and an alkyl halide (alkyl chloride, alkyl bromide or alkiodide). The reaction is carried out at a temperature which increases from room temperature to approximately 150 °C. After cooling, the reaction mixture is introduced
20 in water and the alkylated compound obtained is isolated by filtration.

One alkyl group is introduced into the unit



to be alkylated.

The compound of the following formula (7) is manufactured according to the reaction scheme



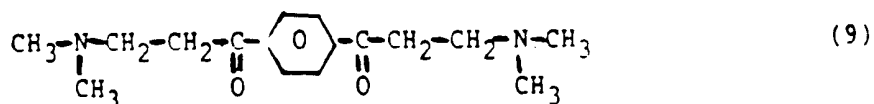
wherein Z is an inorganic acid such as HCl.

40 The reaction is carried out at an increased temperature in the presence of a solvent such as an alcohol and in the presence of an acid such as HCl. The amine according to formula (7) is liberated from the salt form (such as HCl salt) obtained by treating the substance with ammonia and then extracting it using a chlorinated hydrocarbon.

The heterocyclic polymers manufactured according to the invention are doped in a customary manner
45 with iodine (at 100 °C, in the gas phase) or with AsF₅, as has been stated above, and exhibit an electric conductivity which is many orders of magnitude larger, than that of a similar compound which is manufactured in known manner. This means that the polymers manufactured according to the method of the invention have a larger conjugated system. This again emphasizes the importance of the intermediate product of formula (2). The size of the conjugated system of the electrically conductive polymer ultimately
50 obtained is directly dependent on the solubility of the said intermediate product. The solubility can be influenced and, hence, a substantial solubility can be obtained, by the selection of the groups of Ar', Ar'', R present in the intermediate product and the incorporation of other groups.

The electrically conductive heterocyclic polymers obtained according to the present invention can be used advantageously as electric conductors in electromagnetic shielding systems, conductive paints,
55 electrodes, cables, conductive adhesives and oils and fuses as well as semiconductors in transistors and solar cells.

The invention will now be explained in greater detail by means of the exemplary embodiment.

Exemplary embodiment1. Preparation of p-bis (3-dimethylaminopropane-1-on) benzene having the formula

10 A solution of 10.0 g (0.062 mol) p-diacetylbenzene, 11.1 g (0.136 mol) dimethylaminehydrochloride, 13 ml formaldehyde (0.15 mol) and 4 ml of concentrated HCl in 40 ml ethanol is refluxed for several hours. The solid obtained after cooling is separated and recrystallized several times in ethanol water.

15 As a result hereof, 9.8 g of HCl salt of the above-stated compound is obtained. The free amine was obtained by stirring the HCl salt into a 25% NH₄OH solution and, subsequently, extracting it using CH₂Cl₂. After drying and evaporation a solid white substance was obtained having a melting point of 85-87° C.

2. Preparation of poly (1-p-phenyl-1,4-butanedione) of the formula

30 A small quantity of NaCN is added to 5.95 g (21.5 mmol) of the product obtained according to 1, which is dissolved in 80 ml of dimethyl formamide. A solution of 2.89 g (21.5 mmol) of terephthaldehyde in 20 ml dimethyl formamide is added to this solution. After stirring for some time, 50 ml of dimethyl formamide is added to the viscous solution, after which the whole mixture is stirred again at 50-60° C. A sediment is formed. The reaction mixture is pured out in water and filtered off. The yellow solid is successively washed with water, CH₂Cl₂ and ether. After drying, 5.0 g (81%) of polymer of the formula shown above is obtained.

35 Melting point > 212° C.

3. The preparation of poly (p-phenylene-2,5-pyrrole) having the formula

(a) Using liquid ammonium acetate.

A suspension of 1 g of the poly (1-p-phenyl-1,4-butanedione) according to 2 in 20 g of NH₄OAc is stirred for some time at 125° C. The reaction mixture is pured out in water, filtered off and washed with water. The IR spectrum of the solid, brown substance obtained is measured and is found to correspond to the above-stated compound.

50

(b) Using ammonium acetate in dimethyl formamide.

A mixture of 1.7 g of poly (1-p-phenyl-1,4-butanedione) and 20 g of NH₄OAc is dissolved in 100 ml of dimethyl formamide and refluxed for some time. After the mixture is pour out in water the solid, brown substance is filtered off and washed with water. The IR spectrum corresponds to the above-stated poly (p-phenylene-2,5-pyrrole).

55

(c) Using ammonium acetate in acetic acid.

A mixture of 1 g of poly (1-p-phenyl-1,4-butanedione) and 20 g of NH₄OAc in 100 ml of acetic acid

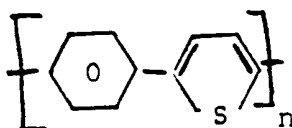
is refluxed for some time. After the mixture is poured out in water the solid obtained is filtered off and washed with water. The IR spectrum corresponds to poly (p-phenylene-2,5-pyrrole).

(d) Using NH_3 in an autoclave.

A test tube comprising 1 g of poly (1-p-phenyl-1,4-butanedione) is introduced into an autoclave. NH_3 gas is introduced into the autoclave. The pressure in the autoclave is 9 bar. The temperature is 250°C .

After several hours the autoclave is cooled and the test tube is removed from the autoclave. The brown solid obtained is analysed by means of, inter alia, measuring the IR spectrum. The analysis corresponds to poly (p-phenylene-2,5-pyrrole).

4. The preparation of poly (p-phenylene-2,5-thiophene) having the formula



(11)

2 g of Lawessons reagent is added to a solution of 1.0 g of poly (1-p-phenyl-1,4-butanedione) in 30 ml of O-dichlorobenzene. The solution is refluxed for some time and subsequently cooled. The solid obtained is stirred into a 20% NaOH solution, filtered off and, in succession, washed with water, CHCl_3 and acetone. The dark-coloured solid is analysed, inter alia, by measuring the IR spectrum. The analysis corresponds to the compound of the above-stated formula.

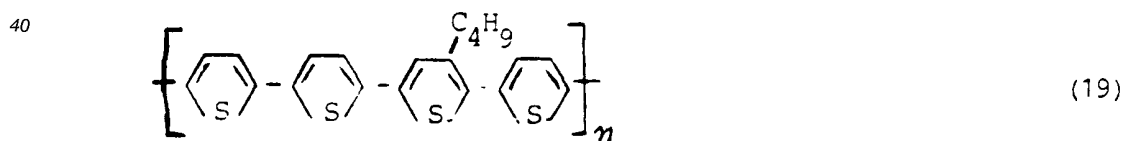
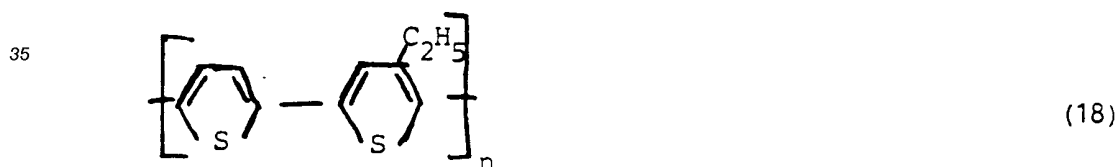
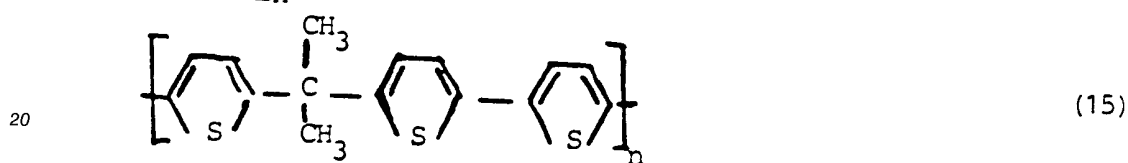
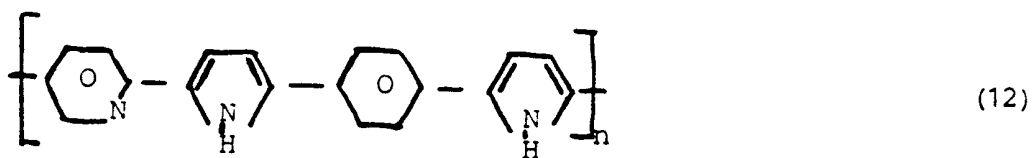
The poly (p-phenylene-2,5-pyrrole) prepared according to the above-described example 3, as well as the poly (p-phenylene-2,5-thiophene) according to example 4 are treated with iodine at 100°C in the gas phase.

The electric conductivity of the polymers which have been doped with J_2 in the above described manner is determined. For poly (p-phenylene-2,5-pyrrole) the conductivity amounts to $1.4 \times 10^{-1} \text{ Scm}^{-1}$.

For the compound poly (p-phenylene-2,5-thiophene) the electric conductivity is $2.5 \times 10^{-2} \text{ Scm}^{-1}$.

Poly (p-phenylene-2,5-thiophene) is a compound which is known per se. If this substance is manufactured according to the well-known Grignard coupling method and doped with J_2 , it has an electric conductivity of $4.10^{-5} \text{ Scm}^{-1}$. Consequently, the poly (p-phenylene-2,5-thiophene) prepared according to the inventive method has a much improved electric conductivity which exceeds that of the substance manufactured in the known manner by a factor of 600.

The heterocyclic polymers of the formulae shown below are manufactured in a manner which corresponds to that described in the above-stated examples 1-4:



45

Claims

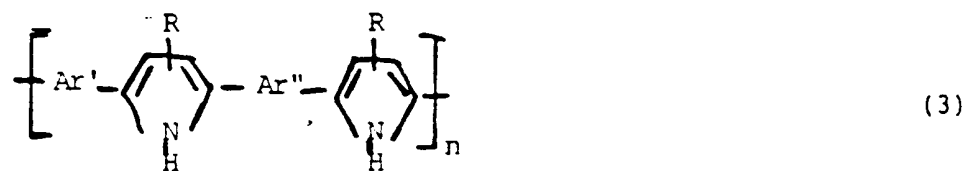
1. A method of manufacturing electrically conductive, heterocyclic polymers comprising a thiophene ring or a pyrrole ring, characterized in that a polymeric, compound comprising keto groups is converted into the desired heterocyclic thiophene polymer or pyrrole polymer by ring closure, which polymer is subsequently rendered electrically conductive in a customary manner by means of doping.
2. A method of manufacturing electrically conductive heterocyclic polymers comprising a thiophene or pyrrole ring as claimed in Claim 1, characterized in that polymers are manufactured which correspond to the formula



wherein Ar' and Ar'' both represent an aromatic group, which groups are the same or different,
 R is a hydrogen atom or an alkyl group having 1-10 C atoms, X is a sulphur atom or the group -NH,
 and
 n is larger than or equal to 25, by reacting a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning, with
 a) NH₃ or a NH₃-producing substance, to obtain a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning,
 or b) a sulphur-phosphor compound, to obtain a compound of the formula



wherein Ar', Ar'', R and n have the above-stated meaning.

40 3. A method as claimed in Claim 2, characterized in that the reaction is carried out at an increased temperature and using NH₃ or ammonium acetate, to which an inert solvent may be added, a compound of formula (3) being formed.

45 4. A method as claimed in Claim 2, characterized in that the reaction at an increased temperature and in the presence of a solvent is carried out using phosphoric sulphide or a Lawessons reagent, a compound of formula (4) being formed.

50 5. A compound of formula



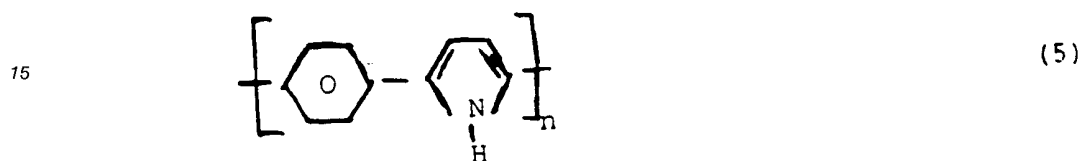
wherein Ar', Ar'', R, X and n have the meaning as stated in Claim 2, and if X is a -NH- group and R is a

H atom, Ar' and Ar'' are not both a pyrrole group, and if X is a -S- atom and R is a H-atom, Ar' and Ar'' are not both a thiophene group or a phenyl group, further excepting linear poly(3-alkyl-2,5-thienylene) polymers having a lower alkyl group and a degree of polymerization n = 25-100.

5 6. A compound as claimed in claim 5, which corresponds to the formula (1) shown in Claim 5, wherein Ar' and Ar'' both have the same meaning and represent a phenyl group, a pyrrole group, a thiophene group or a pyridine group, and wherein R is a hydrogen atom, with the proviso that if Ar' and Ar'' both represent a thiophene or a phenyl group, X is a -NH- group, and if Ar' and Ar'' both represent a pyrrole group, X is a -S- atom.

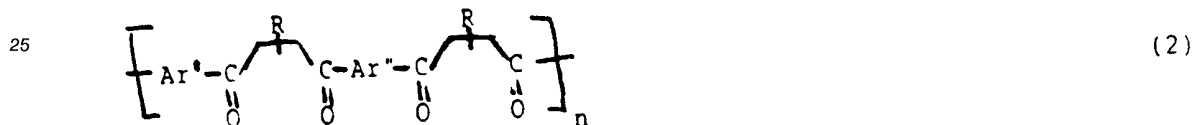
10

7. A compound of the formula



20 wherein n has a value of 25-100.

8. A compound of the formula

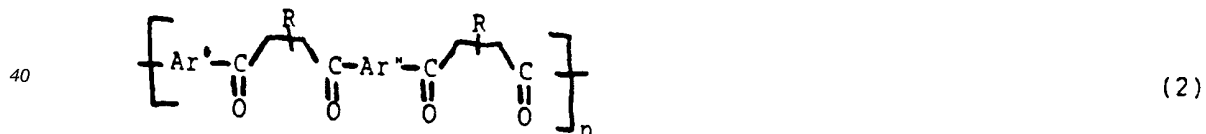


30 wherein Ar', Ar'', R and n have the meaning stated in Claim 2.

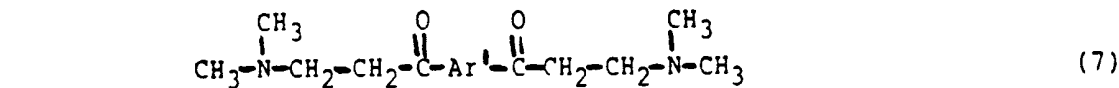
9. A compound as claimed in Claim 8, which corresponds to the formula (2) shown in Claim 8, wherein Ar' and Ar'' have the same meaning and represent a phenyl group, pyrrole group, thiophene group or a pyridine group, and wherein R is a hydrogen atom.

35

10. A method of manufacturing a compound of the formula



45 wherein Ar', Ar'', R and n have the meaning stated in Claim 2, characterized in that a compound of the formula



is made to react with a compound of the formula



to form a polymer of formula (2), wherein R is a hydrogen atom, which polymeric compound may be alkylated, if desired, to form a compound of formula (2), wherein R is an alkyl group.

Patentansprüche

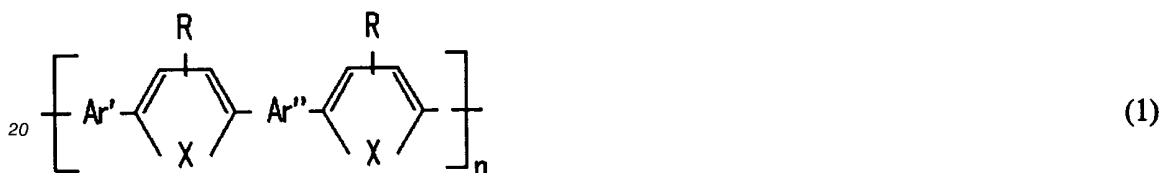
5

1. Verfahren zur Bereitung elektrisch leitender, heterozyklischer Polymere, die einen Thiophen-Ring oder einen Pyrrol-Ring aufweisen, dadurch gekennzeichnet, daß eine Ketogruppen enthaltende polymere Verbindung durch Ringschluß in das erwünschte heterozyklische Thiophenpolymer oder Pyrrolpolymer umgewandelt wird, das danach in einer an sich bekannten Art und Weise durch Dotierung elektrisch leitend gemacht wird.

10

2. Verfahren zur Bereitung elektrisch leitender, heterozyklischer Polymere, die einen Thiophen-Ring oder einen Pyrrol-Ring aufweisen, nach Anspruch 1, dadurch gekennzeichnet, daß Polymere, die der nachstehenden Formel entsprechen:

15



25

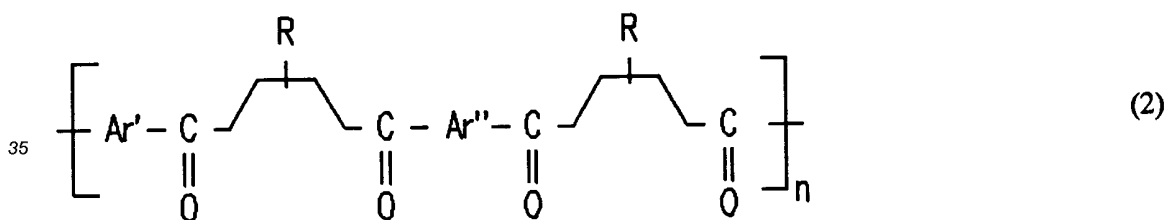
in der: Ar' und Ar'' beide eine aromatische Gruppe darstellen, die einander gleich oder verschieden sind,

R ein Wasserstoffatom oder eine Alkylgruppe mit 1-10 C-Atomen darstellt,

X ein Schwefelatom oder die Gruppe -NH- ist und

n größer als oder gleich 25 ist,

30

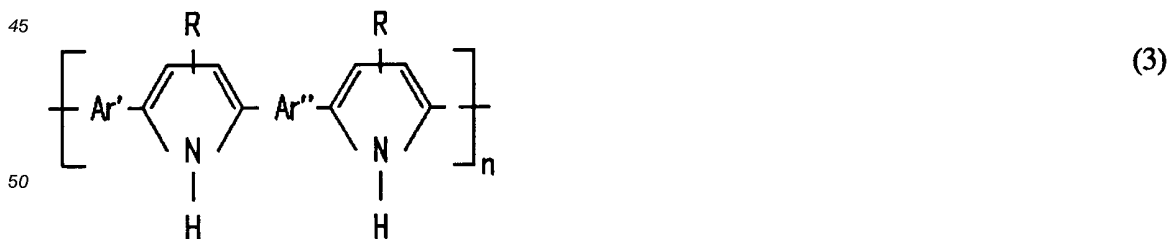


40

in der Ar', Ar'', R und n die obenstehende Bedeutung haben, mit den nachfolgenden Stoffen zum Reagieren gebracht werden:

a) NH₃ oder einem NH₃-erzeugenden Stoff, wobei eine Verbindung der Formel

45



55

erhalten wird,

in der Ar', Ar'', R und n die obenstehende Bedeutung haben, oder

b) einer Schwefel-Phosphorverbindung, wobei eine Verbindung der Formel



10

erhalten wird,
in der Ar', Ar'', R und n die obenstehende Bedeutung haben.

15 3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die Reaktion bei erhöhter Temperatur mit NH₃ oder mit Ammoniumacetat durchgeführt wird, dem gewünschtenfalls ein inertes Lösungsmittel hinzugefügt worden ist, wobei eine Verbindung der Formel (3) gebildet wird.

20 4. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die reaktion bei erhöhter Temperatur und beim Vorhandensein eines Lösungsmittels mit Phosphorpentasulfid oder einem Lawessons Reaktionsmittel durchgeführt wird, wobei eine Verbindung der Formel (4) gebildet wird.

5. Verbindung der nachfolgenden Formel



35 bei der Ar', Ar'', R, X die in Anspruch 2 angegebene Bedeutung haben, und wenn X eine -NH- Gruppe ist und R ein H-Atom darstellt, Ar' und Ar'' nicht beide eine Pyrrol-Gruppe darstellen und wobei in dem Fall, wo X ein -S- Atom darstellt und R ein H-Atom ist, Ar' und Ar'' nicht beide eine Thiophengruppe oder eine Phenylgruppe darstellen, weiterhin mit Ausnahme von linearen Poly (3-Ölquelle-2,5-Thienylen) Polymeren mit einer niedrigeren Alkylgruppe und einem Polymerisationsgrad n = 25-100.

40 6. Verbindung nach Anspruch 5, die der Formel (1) in Anspruch 5 entspricht, wobei Ar' und Ar'' beide dieselbe Bedeutung haben und eine Phenylgruppe, eine Pyrrolgruppe, eine Thiophengruppe oder eine Pyridingruppe darstellen, und wobei R ein Wasserstoffatom ist, unter der Bedingung, daß wenn Ar' und Ar'' beide eine Thiophengruppe oder eine Phenylgruppe darstellen, X eine -NH- Gruppe ist und wenn Ar' und Ar'' beide eine Pyrrolgruppe darstellen, X ein -S- Atom ist.

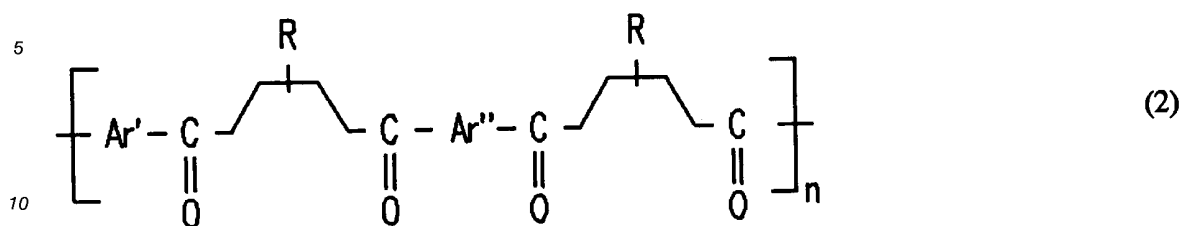
7. Verbindung der Formel

45



55 in der n einen Wert von 25-100 hat.

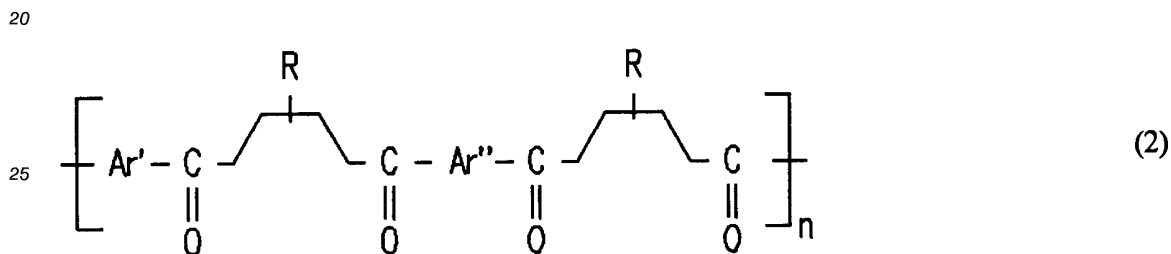
8. Verbindung der Formel



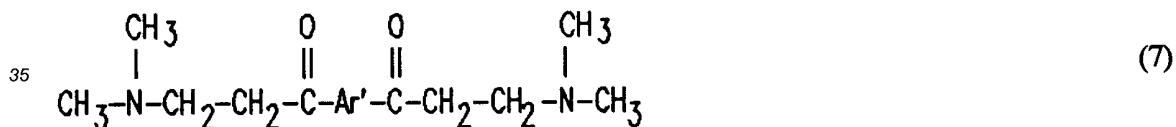
in der Ar', Ar'', R und n die Bedeutung haben wie in Anspruch 2 erwähnt

9. Verbindung nach Anspruch 8, die der Formel (2) in Anspruch 8 entspricht, wobei Ar' und Ar'' dieselbe Bedeutung haben und eine Phenylgruppe, eine Pyrrolgruppe, eine Thiophengruppe oder eine Pyridingruppe darstellen und wobei R ein Wasserstoffatom ist.

10. Verfahren zum Herstellen einer Verbindung der Formel



in der Ar', Ar'', R und n die Bedeutung haben, wie in Anspruch 2 erwähnt, dadurch gekennzeichnet, daß eine Verbindung der Formel



mit einer Verbindung der Formel:



zum Reagieren gebracht wird, wobei ein Polymer der Formel (2) gebildet wird, in der R ein Wasserstoffatom bedeutet, wobei diese polymere Verbindung gewünschtenfalls zu einer Verbindung der Formel (2) alkyliert wird, in der R eine Alkylgruppe darstellt.

Revendications

1. Procédé pour préparer des polymères hétérocycliques électriquement conducteurs comportant un anneau de thiophène ou un anneau de pyrrole, caractérisé en ce qu'un composé polymère comportant des céto-groupes est converti en polymère de thiophène hétérocyclique ou en polymère de pyrrole désirés par fermeture d'anneau, ensuite ledit polymère étant rendu électriquement conducteur de

manière conventionnelle par dopage.

2. Procédé pour préparer des polymères hétérocycliques électriquement conducteurs comportant un anneau de thiophène ou de pyrrole selon la revendication 1, caractérisé en ce que sont fabriqués des polymères correspondant à la formule



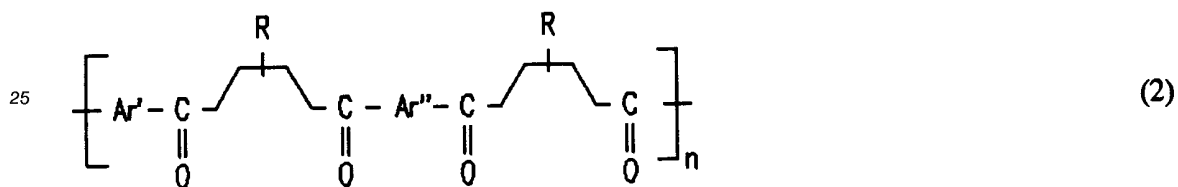
15 dans laquelle Ar' et Ar'' représentent tous les deux un groupe aromatique, lesdits groupes étant identiques ou différents,

R est un atome d'hydrogène ou un groupe d'alkyle comportant 1 à 10 atomes de C,

X est un atome de soufre ou le groupe de -NH-

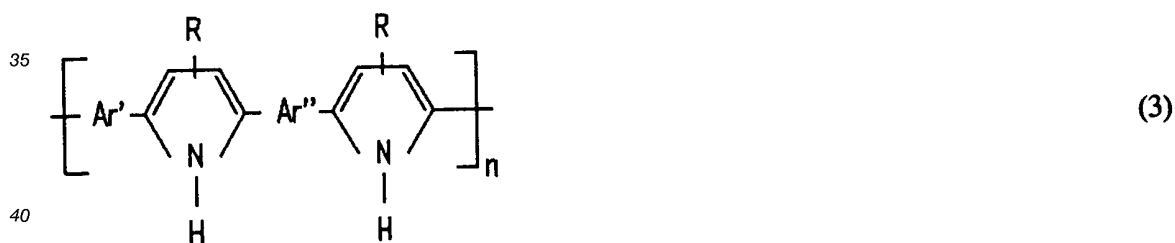
n est supérieur ou égal à 25,

20 en faisant réagir un composé de la formule



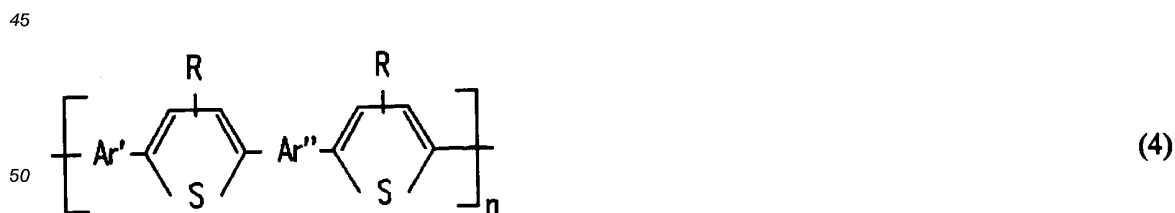
30 dans laquelle Ar', Ar'', R et n ont la signification mentionnée plus haut, avec

a) du NH₃ ou une substance produisant du NH₃ pour obtenir un composé de la formule



dans laquelle Ar', Ar'', R et n ont la signification mentionnée plus haut, ou

b) un composé de soufre et de phosphore pour obtenir un composé de la formule



dans laquelle Ar', Ar'', R et n ont la signification mentionnée plus haut.

- 55 3. Procédé selon la revendication 2, caractérisé en ce que la réaction est effectuée à une température accrue et en ce que l'on utilise du NH₃ ou de l'acétate d'ammonium auquel peut être ajouté un solvant inerte, un composé de la formule (3) étant formé.

4. Procédé selon la revendication 2, caractérisé en ce que la réaction est effectuée à une température accrue et en présence d'un solvant utilisant du sulfure de phosphore ou un réactif de Lawessons, un composé de la formule (4) étant formé.

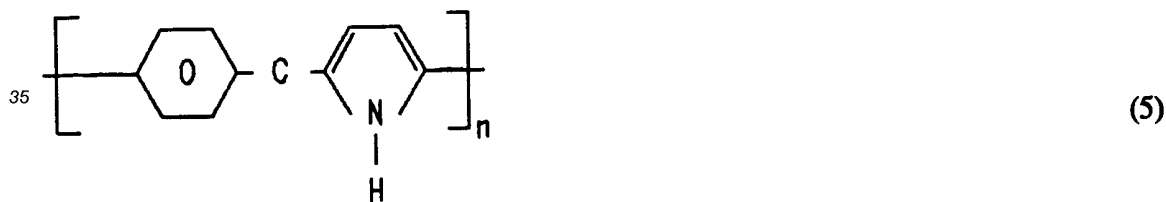
5. Composé de la formule



15 dans laquelle Ar', Ar'', R, X et n ont la signification indiquée dans la revendication 2 et dans laquelle si X est un groupe de -NH et que R représente un atome H, Ar' et Ar'' ne sont pas tous les deux un groupe de pyrrole et dans laquelle si X est un atome de -S- et que R représente un atome de H, Ar' et Ar'' ne sont pas tous les deux un groupe de thiophène ou un groupe de phényle, tout en excluant des polymères poly(3-alkyl-2,5-thiénylène) linéaires de présenter un groupe d'alkyle plus bas et un degré de polymérisation n = 25 - 100.

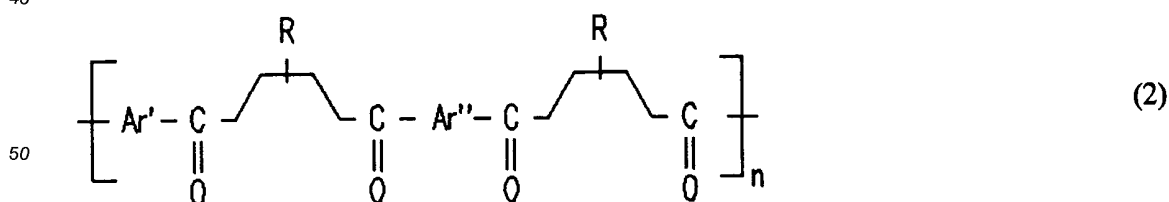
25 6. Composé selon la revendication 5, correspondant à la formule (1) illustrée dans la revendication 5, dans laquelle Ar' et Ar'' ont tous les deux la même signification et dans laquelle ils représentent un groupe de phényle, un groupe de pyrrole, un groupe de thiophène ou un groupe de pyridine, et dans laquelle R est un atome d'hydrogène, sous réserve que si Ar' et Ar'' représentent tous les deux un groupe de thiophène ou un groupe de phényle, X est un groupe de -NH, et si Ar' et Ar'' représentent tous les deux un groupe de pyrrole, X est un atome de -S-.

30 7. Composé selon la formule



40 dans laquelle n a une valeur comprise entre 25 et 100.

45 8. Composé de la formule



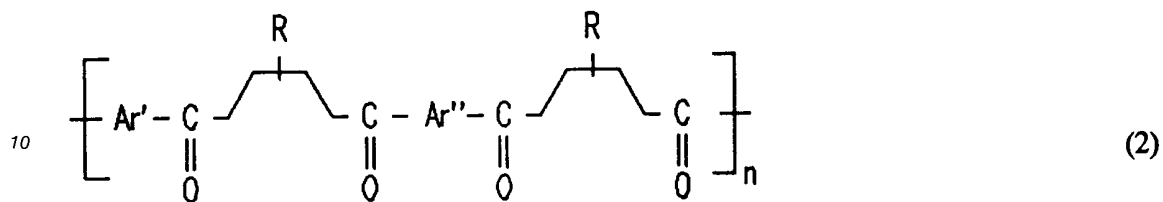
55 dans laquelle Ar', Ar'', R et n ont la signification indiquée dans la revendication 2.

9. Composé selon la revendication 8, correspondant à la formule (2) illustrée dans la revendication 8, dans laquelle Ar' et Ar'' ont la même signification et dans laquelle ils représentent un groupe de phényle, un groupe de pyrrole, un groupe de thiophène ou un groupe de pyridine et dans laquelle R

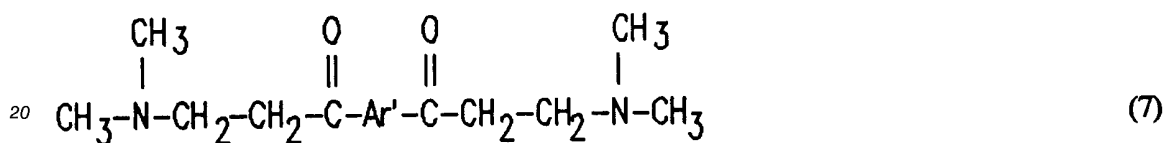
est un atome d'hydrogène.

10. Procédé pour préparer un composé de la formule

5



15 dans laquelle Ar', Ar'', R et n ont la signification indiquée dans la revendication 2, caractérisé en ce que l'on fait réagir un composé de la formule



avec un composé de la formule

25



30

pour former un polymère de la formule (2), dans laquelle R est un atome d'hydrogène, le cas échéant ledit composé polymère étant alkylé pour constituer un composé de la formule (2) dans laquelle R est un groupe d'alkyle.

35

40

45

50

55