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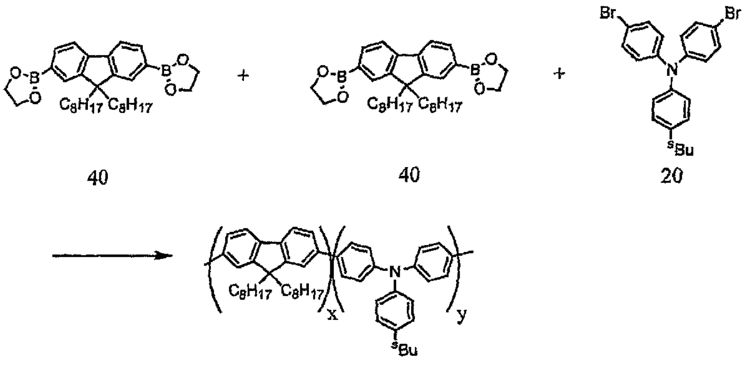

(57) Abstract: A process for preparing a conjugated polymer, which comprises polymerising in a reaction mixture (a) an aromatic monomer having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group; an amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers; and a base in an amount sufficient to convert the boron derivative functional groups into boron anionic groups, characterised in that said reaction mixture further comprises a first solvent and a second solvent with which said first solvent is substantially immiscible and an emulsifier in an amount sufficient to form an emulsion of said reaction mixture.

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CONJUGATED POLYMER PREPARATION VIA SUZUKI-COUPLING IN EMULSION

Background of the Invention

The present invention relates to a process for the preparation of a conjugated polymer, in particular conjugated polymers suitable for use as an active material in organic semiconductor devices including optical devices such as electroluminescent or photovoltaic devices.

Conjugated polyarylenes are widely used as the active material. Examples of such materials include polyfluorenes as disclosed in, for example, WO 99/54385, spirofluorenes as disclosed in, for example, EP 0707020, polyphenylenes as disclosed in, for example, G.Grem, G. Leditzky, B. Ullrich, G. Leising, Adv. Mater. (1992), 4, 36 and phenylene-thienylene copolymers as disclosed in, for example, K.Kaeriyama et al, Synth. Met. (2000), 111-112, 519-522.

Polyarylenes may suitably be prepared by Suzuki or Yamamoto polymerisation. Of these two techniques, Suzuki polymerisation is the only technique that enables exertion of control over the regioregularity of the copolymer. Thus Suzuki polymerisation may be used to generate AB, block or random copolymers depending on the relative quantities of boron and halo monomers used.

It is desirable for polyarylenes for use in the aforementioned optical devices to be of high molecular weight as this improves their processability. High viscosity is also advantageous for certain applications. However, a known drawback of Suzuki polymerisation is the difficulty in reproducibly generating high molecular weight polymers. This has been attributed to the problem of side reactions competing with the polymerisation, e.g. reductive elimination and deboronation of the monomers, which limit the molecular weight of the polymer. These side reactions are initially relatively insignificant but become prevalent at longer reaction times. A fast reaction rate is therefore desirable from the point of view of obtaining high molecular weight material.

US 5777070 discloses the use of the phase transfer catalyst tricaprylylmethyl ammonium chloride in Suzuki polymerisation reactions to facilitate the movement of the reactive boronate species between the organic and aqueous phases of the reaction mixture. In an alternative approach, GB 2360291 describes the use of tetraalkyl ammonium boronate salts soluble in the organic phase such that the polymerisation reaction takes place in a single phase.

It is an object of the invention to provide a reproducible process for preparing high molecular weight conjugated polymers. It is a further object of the invention to reduce reaction time for polymerisation.

Summary of the Invention

In a first aspect, the invention provides a process for preparing a conjugated polymer, which comprises polymerising in a reaction mixture (a) an aromatic monomer having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group; an amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers; and a base in an amount sufficient to convert the boron derivative functional groups into boron anionic groups, characterised in that said reaction mixture further comprises a first solvent and a second solvent with which said first solvent is substantially immiscible and a emulsifier in an amount sufficient to form an emulsion of said reaction mixture.

The term conjugated polymer refers to either a fully conjugated polymer i. e. a polymer which is conjugated along the full length of its chain, or a partially conjugated polymer i.e. a polymer which contains conjugated segments together with non-conjugated segments.

The term emulsion refers to a colloidal suspension comprising a first solvent dispersed within a second solvent, or vice-versa, wherein each of said first and second solvents contain reactive species dissolved therein during at least part of the reaction.

The term emulsifier refers to a substance that coats the particles of the dispersed solvent and prevents coagulation of colloidal particles.

Preferably, the boron anionic group is of formula $-B(OR)_3-$ wherein each R is independently selected from hydrogen or optionally substituted alkyl or aryl and two R groups may be linked.

Preferably, the emulsifier is used in an amount ranging from 1-20% w/v, more preferably in an amount ranging from 1-10% w/v.

Preferably, the first solvent is selected from the group comprising alkylated aromatics. In a particular preferred aspect, the first solvent is toluene. The second solvent is preferably water. The ratio of first solvent to second solvent may range from 0.1:1 up to 10:1 by volume. Preferably, the ratio is in the range 1:1 up to 10:1.

Preferably, the monomers are selected from the group consisting of optionally substituted arylenes, heteroaromatics and fused aromatic systems. In a particularly preferred aspect, at least one of the monomers comprises a triarylamine, a phenylene, a thiophene, a benzothiadiazole or a fluorene wherein each of said monomers is optionally substituted by an alkyl or alkoxy group. Particularly preferred types of monomers include dialkylphenylenes, dialkoxy phenylenes, substituted and non-substituted thiophenes and benzothiadiazoles, and dialkylfluorenes such as 9,9-di-n-octylfluorenes. One or more of the monomers could also be a pre-formed oligomeric or polymeric chain comprising several smaller units with the necessary functional groups provided at the desired positions on the chain.

It is also envisaged that under the appropriate reaction conditions, this invention could also be extended to the use of monomers in which some or all of the functional groups are not directly substituted on an aromatic ring, in particular to other kinds of unsaturated monomers.

The catalyst used in the method of the present invention is preferably a palladium catalyst. The palladium catalyst may be a Pd (0) or Pd (II) species. Particularly preferred catalysts include $Pd(Ph_3P)_4$ and $PdCl_2(Ph_3P)_2$. Typically, the amount of palladium catalyst in the reaction mixture is 0.01 to 1 mol. %, preferably about 0.15 mol. %, based on the total number of moles of monomers used.

The base may be an inorganic base such as a hydroxide, carbonate or hydrogencarbonate of an alkali or alkali earth metal. In a preferred aspect, the base is an organic base, for example a tetraalkylammonium hydroxide, tetraalkylammonium carbonate or tetraalkylammonium hydrogencarbonate.

Preferably, greater than 1 equivalent of base per monomer with a boron functional derivative group or groups is provided in the reaction mixture. More preferably, the quantity of base used is up to 2 equivalents per monomer with a boron derivative functional group or groups

Preferably, the polymer produced is a semiconductive conjugated polymer, in particular a semiconductive conjugated luminescent polymer.

In a second aspect, the invention provides a process for the production of an optical device or acomponent for an optical device, which comprises providing a substrate and producing a polymer in accordance with the process of any one of the preceding claims, whereby the polymer is supported by the substrate. Preferably, the optical device comprises an electroluminescent device or photovoltaic device.

The present invention provides a method for the reproducible production of high molecular weight polymer in a short time. This is achieved by means of the emulsion which greatly increases the surface contact area between the two phases of the reaction mixture as compared with prior art systems.

Brief description of the drawings

The present invention will now be illustrated by way of example only, with reference to the accompanying drawings in which:

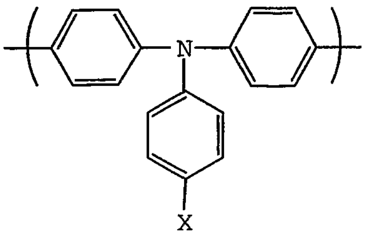
Figure 1 shows the reaction of
Example 1.

Detailed Description of the Invention

The process of the present invention applies to the polymerisation of monomers by Suzuki polymerisation. Accordingly, known methodology for Suzuki polymerisation as disclosed in, for example, WO 00/53656 or the aforementioned prior art, is applicable to the present invention.

The process of the invention may be applied to a wide range of aromatic monomers such as fluorenes, phenylenes, heteroaromatics and triarylamines.

Particularly preferred triarylamine repeat units derived from triarylamine monomers include units of formulae 1-6:



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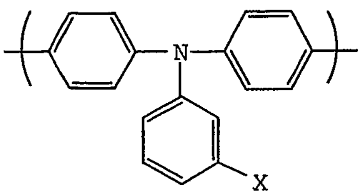

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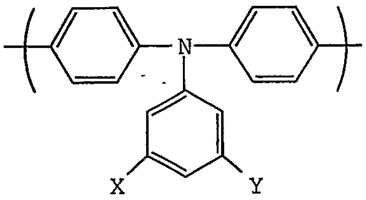

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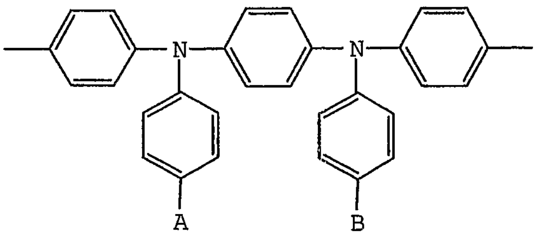

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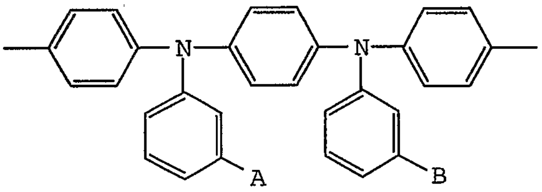

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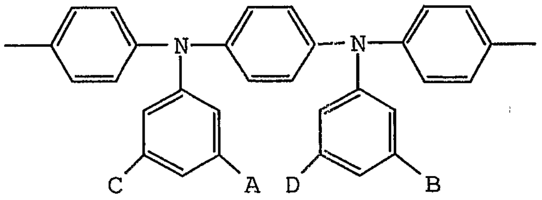

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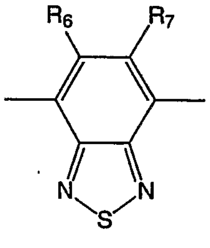
X and Y may be the same or different and are substituent groups. A, B, C and D may be the same or different and are substituent groups. It is preferred that one or more of X, Y, A, B, C and D is independently selected from the group consisting of alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups. One or more of X, Y, A, B, C and D also may be hydrogen. It is preferred that one or more of X, Y, A, B, C and D is independently an unsubstituted, isobutyl group, an n-alkyl, an n-alkoxy or a trifluoromethyl group because they are suitable for helping to select the HOMO level and/or for improving solubility of the polymer.

Particularly preferred heteroaryl repeat units include units of formulae 7-21:



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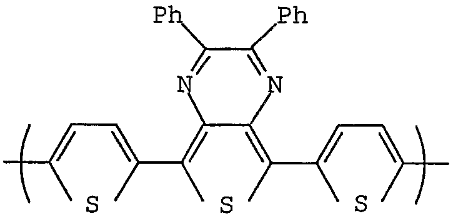
wherein R_6 and R_7 are the same or different and are each independently hydrogen or a substituent group, preferably alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl or arylalkyl. For ease of manufacture, R_6 and R_7 are preferably the same. More preferably, they are the same and are each a phenyl group.



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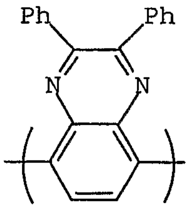

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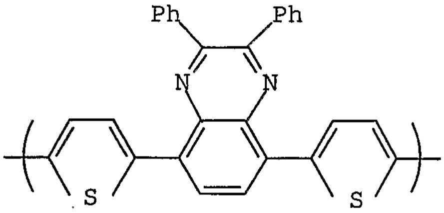

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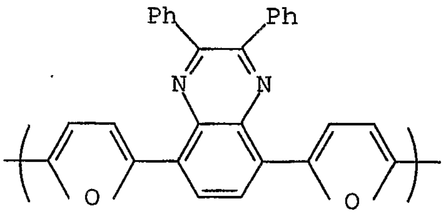

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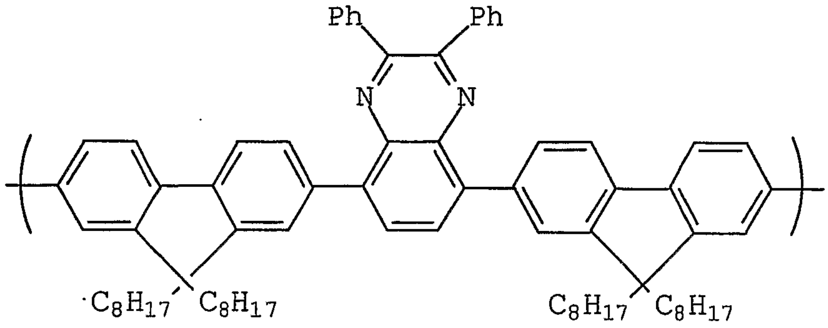

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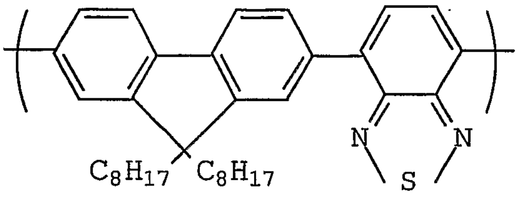

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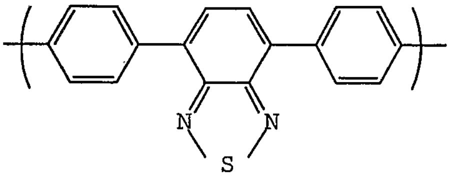

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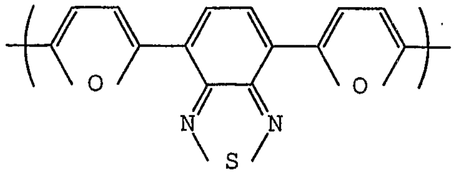

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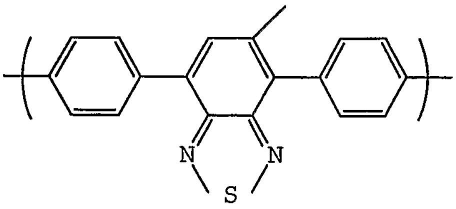

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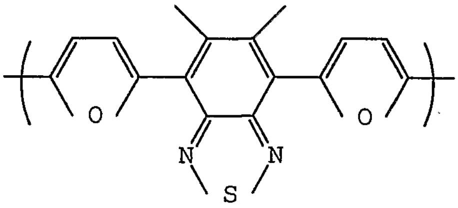

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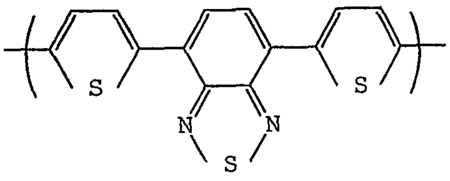

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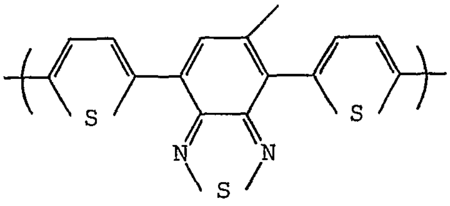

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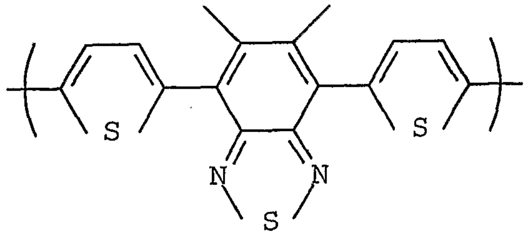

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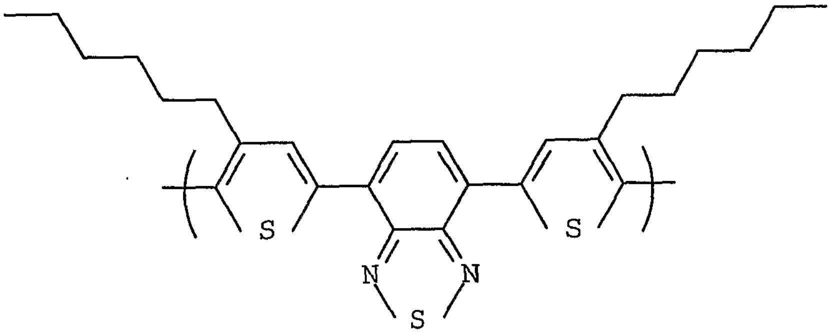

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The first and second solvents may each independently comprise a single solvent or may comprise a blend of miscible solvents.

Examples of specific emulsifiers include the following, available from either Aldrich Chemicals or Raschig GmbH:

poly(ethylene glycol)-block-polypropylene glycol)-block-poly(ethyleneglycol) Mn 4400, Mn 1100, Mn 1900, Mn 8400, Mn 5800, Mn 2800, or Mn 2000; poly(ethylene glycol) 4-nonylphenyl ether acrylate Mn 450, poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether, potassium salt 9 EO/Mole, 20 EO/Mole, poly(ethylene glycol) methyl ether Mn 350, Mn 550, Mn 750, Mn 2000, or Mn 5000; poly(ethylene glycol) n-alkyl 3-sulfopropyl ether, potassium salt 7 EO/mole or 11 EO/mole; poly(ethylene glycol) Mn 10000, Mn 8000, Mn 4600, Mn 3400, Mn 2000, Mn 1500, Mn 1000, Mn 600 or Mn 400; poly(propylene glycol) Mn 425, Mn 725, Mn 1000, Mn 2000, Mn 2700, Mn 3500; poly(propylene glycol) bis(2-aminopropyl ether) Mn 230, Mn 400, Mn 2000 or Mn 4000; poly(propylene glycol-block-polyethylene glycol)-block-polypropylene glycol) bis(2aminopropyl ether) Mn 600, Mn 900 or Mn 2000; poly(propylene glycol-block-polyethylene glycol)-block-polypropylene glycol) Mn 419, Mn 2000, Mn 2700 or Mn 3300; poly(propylene glycol) monobutyl ether Mn 340, Mn 1000, Mn 1200, Mn 2500 or Mn 4000; polyethyleneglycolalpha-(4-nonylphenyl)-omega-3-sulfopropyl-diether, potassium salt; Cocoamidopropylbetaine; Polyethyleneglycol octyl-(3-sulfopropyl)-diether potassium salt; Octaethylene glycol octyl ether; Polyethyleneglycol alkyl-3-sulfopropyl diether, potassium salt; Polyethyleneglycol alkyl-3sulfopropyl diether, potassium salt; Polyethyleneglycol alkyl-3-sulfopropyl diether, potassium salt or N,N-Dimethyl-N-hydrogenated-tallow alkyl-N-(3-sulfopropyl) ammonium betaine.

Polymers preparable according to the invention include, but are not limited to,, straight chain, branched and dendrimeric polymers.

These polymers may have hole transporting, electron transporting and / or emissive properties. The polymer may have one or more of these properties. Where the polymer has more than one of these properties, different properties may be provided by different segments of the polymer, in particular segments of the polymer backbone as described in WO 00/55927 or pendant groups as described in WO 02/26859. Alternatively, if the polymer of the invention has only one or two of the properties of hole transport, electron transport and emission, it may be blended with one or more further polymers having the remaining required property or properties.

As described above, the monomers must each have the appropriate functional groups for the Suzuki reaction. In one arrangement, a first reactive dihalide monomer is polymerised with a second monomer having two boron derivative functional groups. In this arrangement the first and the second monomers may be the same or different.

In a second arrangement, a monomer having a boron derivative functional group and a reactive halide functional group is polymerised to form a homopolymer. It is also possible to form copolymers from this second arrangement simply by polymerising together two or more different types of monomers each containing both functionalities.

Preferably, the reactive halide functional group on the reactive dihalide monomer or the monomer having the reactive halide functional group is Br or I although it is possible to use instead groups such as chlorine, triflate (CF_3SO_3-), tosylate and mesylate. With respect to the boron-derivative functional groups, the boronic acid group is represented by $-B(OH)_2$; the boronic ester group is preferably $-B(OR^1)(OR^2)$ or $-B(OR^5O)$ and the borane group is preferably $-BR_3R_4$, wherein R^1 is a substituted or non-substituted C_1-C_6 alkyl group and R^2 is H or a substituted or non-substituted C_1-C_6 alkyl group; R_3 and R_4 are each independently substituted or nonsubstituted C_1-C_6 alkyl groups, and R_5 is a substituted or non-substituted divalent hydrocarbon radical resulting in a 5 or 6 membered ester ring. Examples of suitable groups as R_5 include substituted or non-substituted C2 or C3 alkylene groups, or substituted or non-substituted ortho-or meta- phenylene groups.

Suitable boronic ester groups include, for example, the products of esterification of the corresponding boronic acid group with monovalent C_1-C_6 alcohols, ethane diols such as ethylene glycol, pinacol, propane diols or ortho aromatic diols such as 1,2-dihydroxybenzene.

Examples

General Method

Apparatus

- 5-neck, single jacketed reaction vessel, fitted with reflux condenser, internal thermometer probe (PT100), nitrogen inlet and exhaust, PTFE-coated stirrer shaft, blade and guide (anchor stirrer) and two stoppers. Each glass joint is coated with a PTFE sleeve. The stirrer motor (mechanically driven, overhead) is equipped with an on-line torque meter. Materials of construction are a glass reactor with glass overhead fittings and ground glass joints; all stirrer shafts, probes and ancillary equipment are PTFE coated mild steel.
- A suitable heater/chiller unit, e.g. Julabo F25 HP programmable, connected to the reactor via M16 fittings and with 2m hoses.
- A suitable stirrer motor for the reactor, e.g. an IKA Eurostar power control visk or any appropriate overhead mechanical stirrer motor.

Procedure

A reaction vessel as described above was charged with 9,9-dioctylfluorene-2,7di(ethylenylboronate) (50.56 g; 95.33 mmol; 1.0 eq.), 2,7-dibromo-9,9'-dioctylfluorene (41.83 g; 76.26 mmol; 0.8 eq.), N,N-bis(4-bromophenyl)-N-(4-sec-butylphenyl)amine (8.76 g; 19.07 mmol; 0.2 eq.), toluene and emulsifier. The mixture was stirred for 5 minutes at room temperature and then degassed for 1 hour with a nitrogen sparge. Dichloro-bis(triphenylphosphine) palladium (0.21 g; 0.3 mmol; 0.003 eq.) was then added and followed by addition of 20% w/w aqueous tetraethylammonium hydroxide (available from Fluka Chemicals) (320 mL) at which point formation of an emulsion was observed. The stirring mixture was heated to arid maintained at reflux until the torque or viscosity no longer increased, or the reaction mixture gelled. In the event of gellation, additional toluene was added.

The reaction was terminated by addition of bromobenzene (1-2ml) followed by stirring at reflux for an hour before adding phenyl boronic acid (1.5-2.0g), after which the mixture was allowed to stir at reflux for a further hour.

The mixture was allowed to cool to room temperature and poured slowly into methanol to precipitate the polymer. Bromobenzene (1-2ml) was added to the mixture, which was allowed to stir at reflux for a further hour before adding phenyl boronic acid (1.5-2.0g), after which the mixture was allowed to stir at reflux for one hour.

The mixture was allowed to cool to room temperature and poured slowly into methanol to precipitate the polymer. The crude polymer was recovered by filtration, washed with fresh methanol polymer and then redissolved in toluene. The toluene solution is warmed to 65°C and washed with diethyldithiocarbamic acid sodium salt solution, dilute hydrochloric acid, aqueous sodium acetate and deionised water. The toluene phase was separated and filtered through Celite 545 (available from Aldrich Chemicals) and eluted with toluene. The toluene eluant was then concentrated in vacuo, the polymer was precipitated from it with methanol, isolated by filtration and dried in vacuo.

The reaction was performed with varying emulsifiers, quantitites of emulsifiers, and quantities of solvents as illustrated in the table below wherein percentage weight of emulsifier per unit volume is calculated by multiplying the weight of emulsifier in grammes by the combined volume of toluene and aqueous base in millilitres.

Example	Emulsifier (g; % w/v)	Toluene (mL)	Product Mp
1	PEG-PPG-PEG Mn 4400 (82g; 10)	500	205,000[1]
2	PEG-PPG-PEG Mn 4400 (20.5g; 2.5)	500	304,000[1]
3	PEG-PPG-PEG Mn 4400 (82g; 6.2)	1000	323,000[1]
4	PEG-PPG-PEG Mn 4400 (82g; 4.5)	1500	379,000[2]
5	PEG-PPG-PEG Mn 4400 (82g; 3.5)	2000	330,000[1]
6	PEG-PPG-PEG Mn 4400 (82g; 2.9)	2500	320,000[1]
7	PEG-4NP-3SPE (30g; 2.2)	1000	302,000[1]

[1] Mp after purification

[2] Mp before end-capping

Claims

1) A process for preparing a conjugated polymer, which comprises polymerising in a reaction mixture (a) an aromatic monomer having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group; an amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers; and a base in an amount sufficient to convert the boron derivative functional groups into boron anionic groups, characterised in that said reaction mixture further comprises a first solvent and a second solvent with which said first solvent is substantially immiscible and an emulsifier in an amount sufficient to form an emulsion of said reaction mixture.

2) A method according to claim 1 wherein the boron anionic group is of formula $-B(OR)_3-$ wherein each R is independently selected from hydrogen or optionally substituted alkyl or aryl and two R groups may be linked.

3) A method according to claim 1 or 2 wherein the emulsifier is a neutral species.

4) A method according to claim 1 or 2 wherein the emulsifier is an anionic species.

5) A method according to claim 3 or 4 wherein the emulsifier is selected from neutral or anionic poly(alkylene glycols) or alkylsulfonate salts.

6) A method according to any preceding claim wherein the emulsifier is used in an amount ranging from 1-20% w/v.

7) A method according to any preceding claim wherein the emulsifier is used in an amount ranging from 1-10% w/v.

8) A method according to claim 1 wherein the first solvent is selected from the group comprising alkylated aromatics.

9) A method according to claim 8 wherein the first solvent is toluene.

10) A method according to claim 1 wherein the second solvent is water.

11) A method according to claim 1 wherein the ratio of first solvent to second solvent is in the range 0.1:1 to 10:1.

12) A method according to any preceding claim wherein the monomers are selected from the group consisting of optionally substituted arylenes, heteroaromatics and fused aromatic systems.

13) A method according to claim 12 wherein at least one of the the monomers comprises a triarylamine, a phenylene, a thiophene, a benzothiadiazole or a fluorene wherein each of said monomers is optionally substituted by an alkyl or alkoxy group.

14) A method according to claim 1 wherein the catalyst comprises a palladium (0) or palladium (II) species.

15) A method according to claim 14 wherein the amount of palladium catalyst in the reaction mixture is 0.01 to 1 mol. % based on the total number of moles of monomers used.

16) A method according to claim 1 wherein the base is an organic base

17) A method according to claim 16 wherein the base is a tetraalkylammonium hydroxide, tetraalkylammonium carbonate or tetraalkylammonium hydrogen carbonate.

18) A method according to any preceding claim wherein greater than 1 equivalent of base per monomer with boron functional derivative group or groups is provided in the reaction mixture.

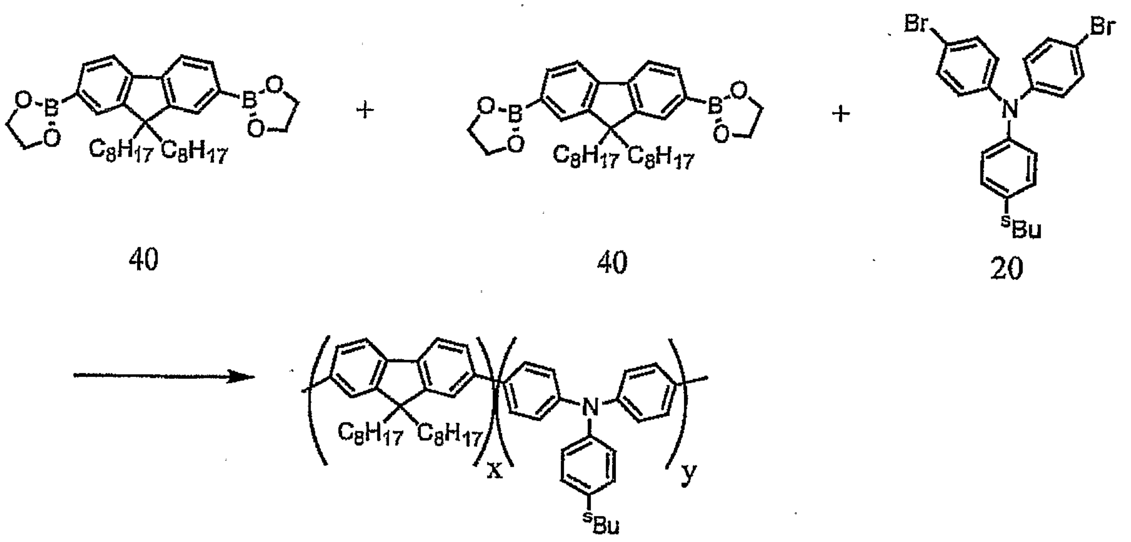
19) A process according to any preceding claim, wherein the polymer produced is a semiconductive conjugated polymer.

20) A process according to claim 19, wherein the semiconductive conjugated polymer is a luminescent polymer.

21) A process for the production of an optical device or acomponent for an optical device, which comprises providing a substrate and producing a polymer in accordance with the process of any one of the preceding claims, whereby the polymer is supported by the substrate.

22) A process according to claim 21, wherein the optical device comprises an electroluminescent device.

Figure 1


C8H17 C8H17
+
40
C8H17 C8H17
+
40
Br
Br
N
sBu
20
C8H17 C8H17
x
N
sBu
y

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/04752

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G61/00 C09K11/06 H05B33/14

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 7 C08G C09K H05B

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) cited in the application column 4, line 28 - line 56; claims 1-19; examples 1-7 ---	1,2,4, 6-22
Y	WO 00 53656 A (TOWNS CARL ROBERT ;DELL RICHARD O (GB); CAMBRIDGE DISPLAY TECH (GB) 14 September 2000 (2000-09-14) cited in the application page 2 -page 3 page 7 -page 8 --- -/--	1,2,4, 6-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 14 March 2003	Date of mailing of the international search report 28/03/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Marsitzky, D

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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