

(43) International Publication Date
24 May 2012 (24.05.2012)

(51) International Patent Classification:

C09D 5/24 (2006.01) *H01B* 1/20 (2006.01)
C09D 163/02 (2006.01) *C08L* 63/00 (2006.01)
C08L 65/00 (2006.01) *C09D* 133/14 (2006.01)

(21) International Application Number:

PCT/MY2011/000137

(22) International Filing Date:

23 June 2011 (23.06.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PI2010005363 15 November 2010 (15.11.2010) MY

(71) Applicant (for all designated States except US): **MIMOS BERHAD** [MY/MY]; Mimos Berhad, Technology Park Malaysia, Kuala Lumpur, 57000 (MY).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MOHD RAIS, Ahmad** [MY/MY]; Mimos Berhad, Technology Park Malaysia, Kuala Lumpur, 57000 (MY).

(74) Agent: **NORUNNUHA, Nawawi**; Norunnuha Sdn Bhd, No 17-2 Jalan Medan Pusat 2d, Persiaran Bangi, Bandar Baru Bangi, Selangor 43650 (MY).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,

DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

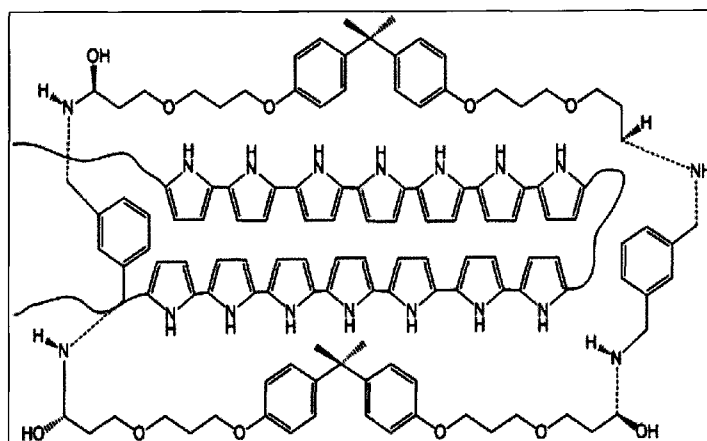
Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: COMPOSITION OF SOLVENT CASTING SOLUTION COMPRISING POLYPYRROLE POWDER FOR USE AS A TRANSDUCER IN BIOCHEMICAL SENSOR APPLICATIONS

**FIG. 2**

(57) Abstract: The present invention relates to a composition of solvent cast solution which comprising an impedance organic binder, a purified diamine crosslinker, a polypyrrole powder, an organic sulfonate salt, and a polar solvent. The solvent cast solution is used as a transducer in bio-chemical sensor applications. The solvent cast solution is usable for the preparation of ion selective electrode (ISE) chemical sensor, ion sensitive field effect transistor (ISFET) chemical sensor, amperometric biosensor, conductometric sensor, voltammetric sensor, reference electrode or fuel cell.

Description

COMPOSITION OF SOLVENT CASTING SOLUTION COMPRISING POLYPYRROLE POWDER FOR USE AS A TRANSDUCER IN BIOCHEMICAL SENSOR APPLICATIONS

Technical Field

Technical Field

- [1] The present invention relates to a composition of solvent casting solution. More particularly, the solvent cast solution is used as a transducer in bio-chemical sensor applications.

Background Art

Background Art

- [2] Polypyrrole (PPy) has been widely used as transducer or conducting material in chemical sensors. In most applications, pyrrole monomer is electropolymerized from doped electrolyte solution. PPy grows well on screen-printed carbon surface, shows good adhesion with the electrode surface, and more importantly affords reproducible sensing characteristics.
- [3] Conductive polymer transducer such as polypyrrole (PPy) are usually electrochemically deposited on electrode surface via electrochemical method. On screen printed carbon surface the desired thickness of PPy transducer can be deposited by electropolymerization within minutes. On metal surface such as platinum or stainless steel much longer electropolymerization time is required to achieve the targeted thickness - hours are sometimes needed to complete the polymerization.
- [4] However, electropolymerization of pyrrole is not an option when the electrical contacts are not accessible or prone to electrical shorting when exposed to pyrrole electrolyte. In this case drop coating of polypyrrole solution is desirable.
- [5] Spin or drop coating of polypyrrole solution onto electrode surface is preferred when electropolymerization is not possible due to miniature size of the electrode, inaccessability of the electrical contact or electrical shorting of the contact pads in pyrrole monomer electrolyte solution.
- [6] Due to that, there is a need in the art to provide a solution casting polypyrrole composition that can give reproducible electrochemical characteristics of the polypyrrole transducer layer for bio-chemical sensor applications.

Disclosure of Invention

Technical Problem

[7]

Technical Solution

[8]

Summary

- [9] According to a first aspect of the present invention, there is provided a solution casting polypyrrole composition comprising an impedance organic binder; a purified diamine crosslinker; a polypyrrole powder; an organic sulfonate salt; and a polar solvent. The provision of the method is advantageous as it results in producing reproducible electrochemical characteristics of the polypyrrole transducer layer for biochemical sensor applications.
- [10] According to a second aspect of the present invention, there is provided a method for purifying the diamine crosslinker comprising the steps of diluting the diamine crosslinker with diethyl ether and obtain a mixture; washing the mixture with saturated sodium bicarbonate and brine solution; drying the mixture with sodium sulfate followed by magnesium sulfate; and extracting the mixture by distillation under reduced pressure over a drying agent and obtaining a purified diamine crosslinker.
- [11] According to a third aspect of the invention, there is provided a method for producing the solvent cast solution comprising the steps of adding a purified diamine crosslinker and impedance organic binder into a polar organic solvent to obtain a first mixture; adding a polypyrrole powder and an organic sulfonate salt into a polar solvent to obtain a second mixture; stirring the first and second mixture at about 10 to 60 minutes; and mixing the first and second solution followed by stirring the mixture at about 10 to 60 minutes and obtaining a solvent cast solution.
- [12] According to a fourth aspect of the invention, there is provided a product produced by the solvent cast solution process is usable for the preparation of ion selective electrode (ISE) chemical sensor, ion sensitive field effect transistor (ISFET) chemical sensor, amperometric biosensor, conductometric sensor, voltammetric sensor, reference electrode or fuel cell.

Description of Drawings

- [13] For a fuller understanding of the nature of the present invention, reference should be made to the following detailed description taken in connection with the accompanying drawings in which:
- [14] **FIG.1:** illustrates a solvent cast polypyrrole with acrylate copolymer binder of the present invention.
- [15] **FIG.2:** illustrates a solvent cast polypyrrole with Bisphenol A propoxylate diglycidyl ether binder of the present invention.
- [16] **FIG.3:** illustrates a high polarity crosslink-able copolymer which is methyl methacrylate-glycidyl methacrylate-tetrahydrofurfuryl acrylate (MGT)
- [17] of the present invention.
- [18] **FIG.4:** illustrates a chemical structure of Bisphenol A propoxylate diglycidyl ether

resin of the present invention.

[19] **FIG.5:** illustrates a preferred alkyl and aromatic diamine crosslinkers of the present invention.

[20] **FIG.6:** illustrates a method for purifying a diamine crosslinker of the present invention.

[21] **FIG.7:** illustrates a chemical structure of alkyl benzene sulfonate salt additive of the present invention

[22] **FIG.8:** illustrates a cyclic voltammetry measurement of polypyrrole- Bisphenol A Propoxylate Diglycidyl ether solution of the present invention.

[23] **FIG.9:** illustrates a cyclic voltammetry measurement of polypyrrole-MGT622 solution of the present invention.

[24] **FIG.10:** illustrates a method for producing a solvent cast solution of the present invention.

[25]

[26] **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

[27] In order to prepare homogenous composition of polypyrrole the first requirement would be to get good solubility of polypyrrole in suitable solvent. While custom-made doped polypyrrole have been shown to exhibit high solubility in organic or aqueous media, commercially available and commonly used doped polypyrroles (in fine powder form) are insoluble in water or polar solvents. The polar solvent in the present invention is selected from the group of methanol, ethanol, propanol, *iso*-propanol, tri-fluoroethanol, 2-methoxyethanol, diethylether, tetrahydrofuran, acetonitrile, dimethyl-sulfoxide, dimethyl formamide, propylene carbonate or water.

[28] Another requirement for preparing polypyrrole composition for modifying electrode surface is the adhesion of the dried PPy on wide range of possible preferred electrode surface such as platinum, carbon, silver, silicon nitride, silicon, polysilicon, silicon oxide, polyester, FR4 or glass. A homogenous PPy composition is desirable in order to maintain and stabilize the electrochemical characteristics of the PPy transducer layer. Conductive binder that can glue the PPy fibers together, as well as bonding to electrode surface is needed. **FIG.1** shows the chemical structure of a solvent cast conductive polypyrrole with acrylate copolymer binder.

[29] Yet another requirement is the adhesion of the cured PPy conductive layer with a wide variety of plausible polymeric sensing membranes such as PVC, acrylate, urethane or silicone rubber. It is desirable for the sensing membrane of choice to have natural binding to the dried PPy transducer layer.

[30] In one embodiment, the present invention provides a composition of solvent cast solution which comprises an impedance organic binder, a purified diamine crosslinker, a polypyrrole powder, an organic sulfonate salt, and a polar solvent. Preferably, the

impedance organic binder ranges from 5 to 20 wt. %, the purified diamine crosslinker ranges from 5 to 20 wt. %, the polypyrrole powder ranges from 5 to 20 wt. %, the organic sulfonate salt ranges from 0.5 to 5 wt. % and balance is the polar solvent.

- [31] The low impedance organic binder with diamine crosslinker was used as binder for doped polypyrrole powder dissolved in polar solvent or the mixture of polar solvent and deionized water. The impedance organic binder is selected from the group of cellulose acetate, ethyl cellulose, cellulose, Bisphenol A propoxylate diglycidyl ether, methyl methacrylate-glycidyl methacrylate-tetrahydrofurfuryl acrylate copolymer, or glycidyl methacrylate-tetrahydrofurfuryl acrylate copolymer. **FIG.2** shows the chemical structure of a solvent cast conductive polypyrrole with Bisphenol A propoxylate diglycidyl ether binder.
- [32] For diamine crosslinker, it is selected from the group of *meta*-xylylenediamine, *para*-xylylenediamine, *para*-phenylenediamine, 1,3-diaminopropane or 1,4-diaminobutane.
- [33] When the electrode surface is too small or when immersion of electrode contacts into electrolyte results in shorting or when the electrode contacts are inaccessible for electropolymerization, drop coating method is a technique of choice for introducing polypyrrole transducer layer for bio-chemical sensors. The PPy solution is homogenous and not too viscous to give reproducible results and facilitate dispensing. Moreover, it is important that the binding component be able hold the polypyrrole active component together while maintaining its conductive characteristic and reduction-oxidation properties. **FIG.3** shows the chemical structure of a high polarity crosslink-able copolymer which is methyl methacrylate-glycidyl methacrylate-tetrahydrofurfuryl acrylate (MGT). The copolymer contains oxirane group that rings open upon mixing with primary diamine - thus irreversibly crosslinking the copolymer upon treatment of gentle heating.
- [34] Furthermore, mild temperature (near ambient temperature) curing within short time will afford high throughput. Adhesion of the cured PPy transducer film on a wide range of possible conductive underneath layer such as carbon, silver, platinum or gold, as well as, the binding of a wide variety of sensing membrane such as PVC, acrylate, urethane and silicone rubber, is a crucial criterion for the PPy solvent casting solution.
- [35] Commercially available epoxy resin, Bisphenol A propoxylate diglycidyl ether is also attractive due to its cost benefit and ease of handling. **FIG.4** illustrates the chemical structure of Bisphenol A propoxylate diglycidyl ether resin.
- [36] Primary alkyl or aromatic diamine are preferred crosslinkers for heat curing the above acrylate copolymer and Bisphenol A epoxy resin. The main reason for using diamine includes its availability in liquid form, ease of purification and mild curing temperature. Moreover, the diamine gives sufficient surface to accommodate the PPy strands and polymeric membrane network. Diamine crosslinkers as illustrates in **FIG.5**

, were purified by vacuum distillation over barium oxide or calcium hydride. For the straight chain alkyl diamine the preferred number of methylene units are two to six ($n = 0$ to 4).

[37] **FIG.6** illustrates a schematic diagram of the method for purifying a diamine crosslinker which comprises the steps of diluting the diamine crosslinker with diethyl ether and obtain a mixture; washing the mixture with saturated sodium bicarbonate and brine solution; drying the mixture with sodium sulfate followed by magnesium sulfate; and extracting the mixture by distillation under reduced pressure over a drying agent and obtaining a purified diamine crosslinker. The drying agent in the method for purifying a diamine crosslinker of the present invention is selected from the group of barium oxide, phosphorus pentoxide or calcium hydride.

[38] One of the compositions of the solvent cast solution is the organic sulfonate salt which is selected from the group of *para*-toluene sulfonate, dodecyl benzene sulfonate, camphor sulfonate or Nafion. Preferably, para-alkyl benzene sulfonate salt is used, where the number of methylene carbons are 0 to 12 and the metal counterion is sodium or potassium, is added to facilitate dissolution of polypyrrole in alcohol-water solvent. The chemical structure of *para*-toluene sulfonate derivative is as illustrates in **FIG.7**.

[39] The present invention will be explained in more detail through the examples below. The examples is presented only to illustrate the preferred embodiments of the present invention and not intended in any way to limit the scope of the present invention.

[40] **Example 1**

[41] **Preparation of Polypyrrole Composition with Bisphenol A Propoxylate Diglycidyl Ether-Diamine Binder**

[42] Bisphenol A propoxylate diglycidyl ether and *m*-xylylene diamine were procured from Aldrich chemical company. The Bisphenol resin was used as received, whereas, *m*-xylylene diamine was distilled under reduced pressure over barium oxide.

[43] Doped polypyrrole fine black powder were received from the same supplier and used without further purification. Bisphenol A diglycidyl resin 100 mg was transferred into a glass vial and 50 μ L of freshly distilled *m*-xylylene diamine crosslinker was added into the resin, and the mixture diluted with methanol-deionized water (50/50 by volume) mixture to give 20% solution of the polymer. The vial tightly capped and the mixture shaken vigorously to inspect readiness to form homogenous cocktail. The mixture was further sonicated for additional 30 minutes. Doped polypyrrole powder (300 mg) and 50 mg sodium *p*-toluene sulfonate were added into a glass vial containing 2 mL of 50/50 (by volume) mixture of methanol-deionized water.

[44] The vial was tightly capped and vigorously shaken to check the readiness of dissolution and the mixture sonicated for one hour. The contents of the two vials

containing Bisphenol-diamine solution and polypyrrole-salt solution were combined and the final mixture was sonicated for additional 2 hours until homogenous solution was produced. The solvent cast polypyrrole solution is stored at 4 °C before use.

- [45] The solvent cast polypyrrole solution (5 μ L) was drop coated onto-screen printed carbon electrode and the solvent evaporated under nitrogen atmosphere for 1 hour. Cyclic voltammetry of the solvent cast polypyrrole was performed with Metrohm Autolab system in 0.1M potassium chloride solution with silver-silver chloride double - junction reference electrode and platinum counter electrode. The result is shown in FIG.8.

- [46] **Example 2**

- [47] **Preparation of Polypyrrole Cocktail with Methyl Methacrylate-Glycidyl Methacrylate-Tetrahydrofurfuryl Acrylate (MGT 622) Copolymer-Diamine Binder**

- [48] Doped polypyrrole fine powder and *m*-xylylene diamine were procured from Aldrich chemical company. The doped polypyrrole was used without further purification. *m* - Xylylene diamine was distilled under reduced pressure over barium oxide. Copolymer of methyl methacrylate-Tetrahydrofurfuryl Acrylate (MGT622) was freshly prepared from 6 mL of methyl methacrylate, 2 mL of glycidyl methacrylate and tetrahydro-furfuryl acrylate and 3.7 mg of benzoyl peroxide, refluxed at 95 °C for 7 hours.

- [49] 100 mg of MGT622 copolymer was transferred into a glass vial and 50 μ L of freshly distilled *m*-xylylene diamine crosslinker was added into the resin, and the mixture diluted with methanol-deionized water (50/50 by volume) mixture to give 20% solution of the polymer. The vial tightly capped and the mixture shaken vigorously to inspect readiness to form homogenous cocktail. The mixture was further sonicated for additional 30 minutes.

- [50] Doped polypyrrole powder (300 mg) and 50 mg sodium *p*-toluene sulfonate were added into a glass vial containing 2 mL of 50/50 (by volume) mixture of methanol-deionized water. The vial was tightly capped and vigorously shaken to check the readiness of dissolution and the mixture sonicated for one hour. The contents of the two vials containing Bisphenol-diamine solution and polypyrrole-salt solution were combined and the final mixture was sonicated for additional 2 hours until homogenous cocktail was produced. The solvent cast polypyrrole cocktail is stored at 4 °C before use.

- [51] Cyclic voltammetry of the solvent cast polypyrrole was performed with Metrohm Autolab system in 0.1M potassium chloride solution with silver-silver chloride double - junction reference electrode and platinum counter electrode. The result is shown in FIG.9.

- [52] **FIG.10** illustrates the schematic diagram of method for producing the solvent cast

solution which comprises the steps of adding a purified diamine crosslinker and impedance organic binder into a polar organic solvent to obtain a first mixture; adding a polypyrrole powder and an organic sulfonate salt into a polar solvent to obtain a second mixture; stirring the first and second mixture at about 10 to 60 minutes; and mixing the first and second solution followed by stirring the mixture at about 10 to 60 minutes and obtaining a solvent cast solution.

[53] The solvent cast solution produced is usable for the preparation of ion selective electrode (ISE) chemical sensor, ion sensitive field effect transistor (ISFET) chemical sensor, amperometric biosensor, conductometric sensor, voltammetric sensor, reference electrode or fuel cell.

[54] Although the invention has been described with reference to particular embodiment, it is to be understood that the embodiment is merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiment that other arrangements may be devised without departing from the scope of the present invention as defined by the appended claims.

Best Mode

[55]

Mode for Invention

[56]

Industrial Applicability

[57]

Sequence List Text

[58]

Claims

[Claim 1]

1. A composition of a solvent cast solution comprising
an impedance organic binder;
a purified diamine crosslinker;
a polypyrrole powder;
an organic sulfonate salt; and
a polar solvent.
2. A composition of a solvent cast solution as claimed in Claim 1,
wherein the impedance organic binder ranges from 5 to 20 wt. %, the
diamine crosslinker ranges from 5 to 20 wt. %, the polypyrrole powder
ranges from 5 to 20 wt. %, the organic sulfonate salt ranges from 0.5 to
5 wt. % and balance is the polar solvent.
3. A composition of a solvent cast solution as claimed in Claim 1 or 3,
wherein the impedance organic binder is selected from the group of
cellulose acetate, ethyl cellulose, cellulose, Bisphenol A propoxylate
diglycidyl ether, methyl methacrylate-glycidyl methacrylate-
tetrahydrofurfuryl acrylate copolymer, or glycidyl methacrylate-
tetrahydrofurfuryl acrylate copolymer.
4. A composition of a solvent cast solution as claimed in Claim 1 or 3,
wherein the diamine crosslinker is selected from the group of *meta* -
xylylenediamine, *para*-xylylenediamine, *para*-phenylenediamine,
1,3-diaminopropane or 1,4-diaminobutane.
5. A composition of a solvent cast solution as claimed in Claim 1 or 3,
wherein the organic sulfonate salt is selected from the group of *para*-
toluene sulfonate, dodecyl benzene sulfonate, camphor sulfonate or
Nafion.
6. A composition of a solvent cast solution as claimed in Claim 1 or 2,
wherein the polar solvent is selected from the group of methanol,
ethanol, propanol, *iso*-propanol, trifluoroethanol, 2-methoxyethanol, di-
ethylether, tetrahydrofuran, acetonitrile, dimethylsulfoxide, dimethyl
formamide, propylene carbonate or water.
7. A method for purifying the diamine crosslinker as claimed in Claim
1 comprising the steps of:
 - a) diluting the diamine crosslinker with diethyl ether and obtain a
mixture;
 - b) washing the mixture with saturated sodium bicarbonate and brine
solution;

c) drying the mixture with sodium sulfate followed by magnesium sulfate; and

d) extracting the mixture by distillation under reduced pressure over a drying agent and obtaining a purified diamine crosslinker.

8. A method as claimed in Claim 7, wherein the drying agent is selected from the group of barium oxide, phosphorus pentoxide or calcium hydride.

9. A method for producing the solvent cast solution comprising the steps of:

a) adding a purified diamine crosslinker and impedance organic binder into a polar organic solvent to obtain a first mixture;

b) adding a polypyrrole powder and an organic sulfonate salt into a polar solvent to obtain a second mixture;

c) stirring the first and second mixture at about 10 to 60 minutes; and

d) mixing the first and second solution followed by stirring the mixture at about 10 to 60 minutes and obtaining a solvent cast solution.

A product produced by a process of Claim 9, wherein the solvent cast solution produced is usable for the preparation of ion selective electrode (ISE) chemical sensor, ion sensitive field effect transistor (ISFET) chemical sensor, amperometric biosensor, conductometric sensor, voltammetric sensor, reference electrode or fuel cell.

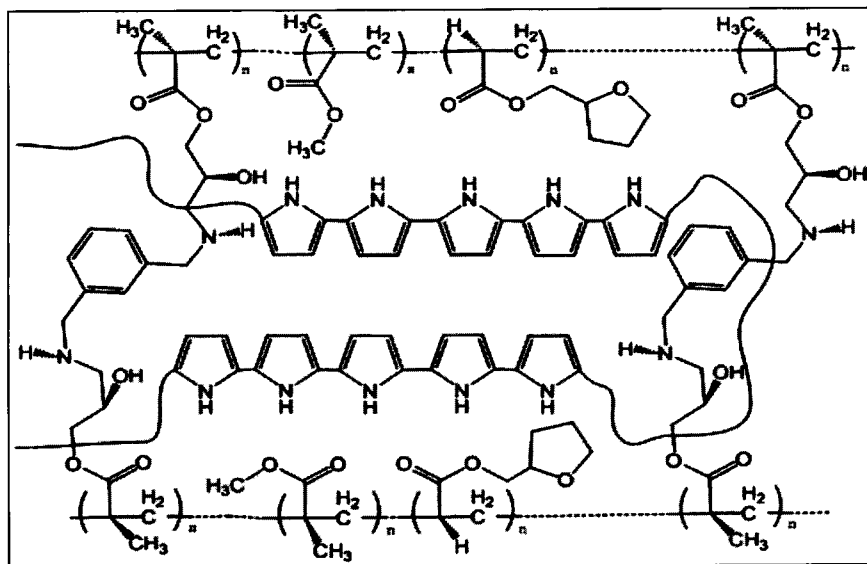


FIG. 1

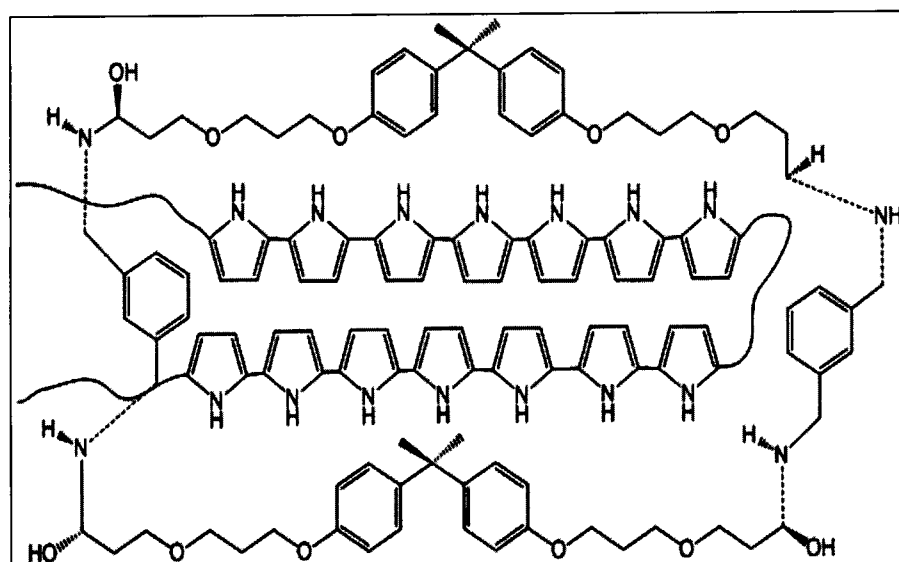


FIG. 2

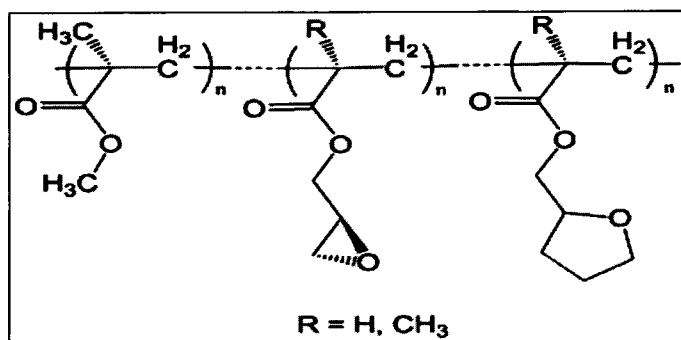


FIG. 3

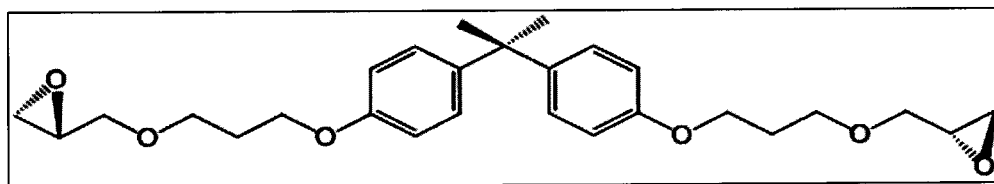


FIG. 4

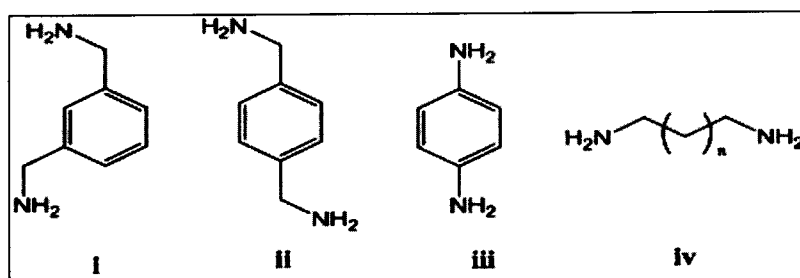
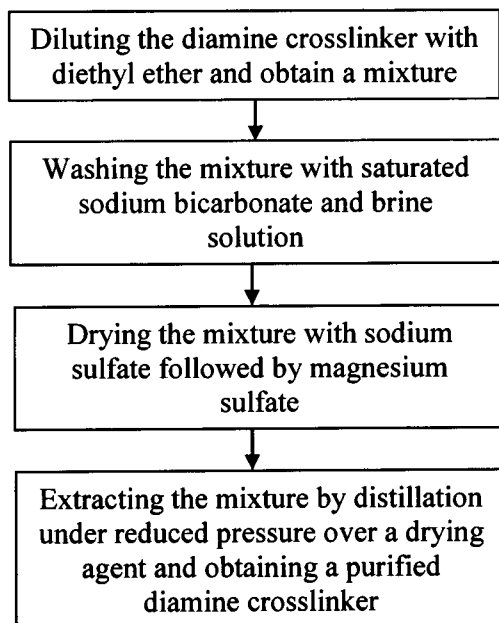
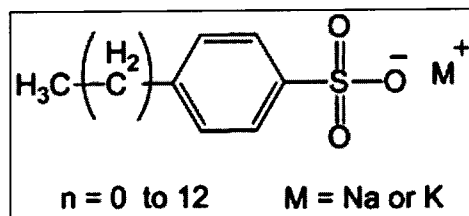


FIG. 5

**FIG. 6****FIG. 7**

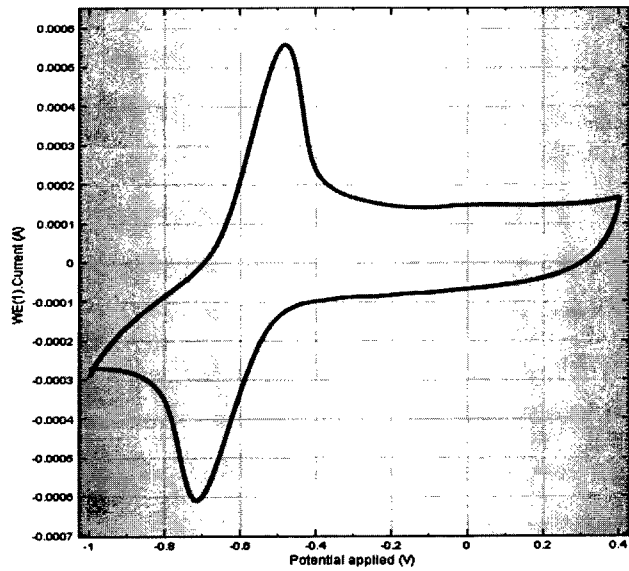


FIG. 8

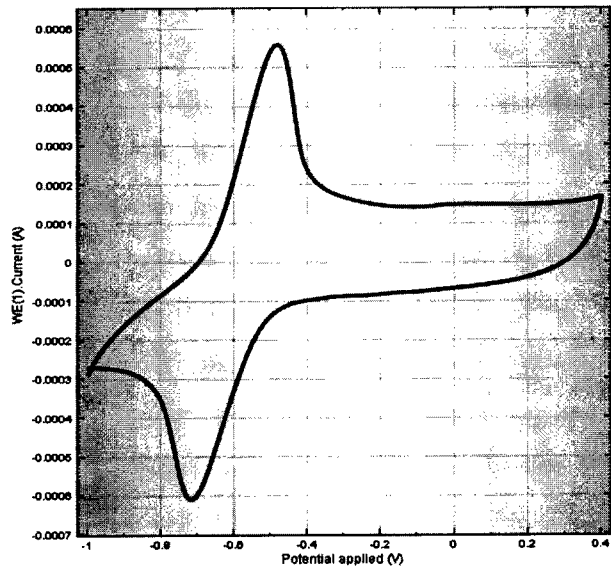
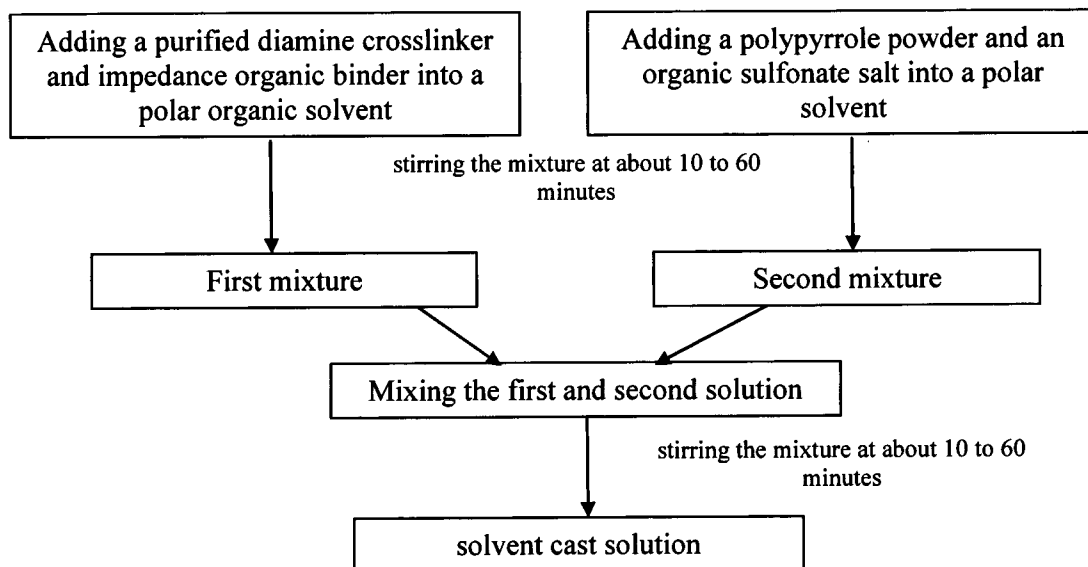


FIG. 9

**FIG. 10**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/MY2011/000137

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C09D 5/24 (2006.01)

C09D 163/02 (2006.01)

C08L 65/00 (2006.01) H01B 1/20 (2006.01)

C08L 63/00 (2006.01)

C09D 133/14 (2006.01)

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)

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 practicable, search terms used)

Wpids, epodoc, caplus: polypyrrole, epoxy, epoxies, +glycidyl+, bisphenol, cellulose+, cross_link?, +diamine, curable, solvent, coating, dispersion, sensor?, transduc+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FOURNIER J. et al., "Percolation Network of Polypyrrole in Conducting Polymer Composites", Synthetic Metals, 1997, vol 84, pages 839-840. See section 2, Figure 2	1-10
X	Derwent Abstract Accession Number: 2010-P52544, CN 101851459 A, (RIZHAO JUNQING ENERGY TECHNOLOGY MATERIAL CO LTD), 6 October 2010 See abstract	1-10
X	US 4697000 A (WITUCKI et al.) 29 September 1987 See col 3 line 20-52, example VI	1-10



Further documents are listed in the continuation of Box C



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"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

01 September 2011

Date of mailing of the international search report

01.09.2011

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustalia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer

KATHY WONG

AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)

Telephone No : +61 2 6283 2737

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2011/000137

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

Patent Document Cited in Search Report			Patent Family Member				
CN	101851459	NONE					
US	4697000	EP	0267392	JP	63101415	US	4617228
		US	4696835	US	4697001	US	4710401
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
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