(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 August 2005 (11.08.2005)

PCT

(10) International Publication Number
WO 2005/073262 A1

(51) International Patent Classification[7]: C08F 271/02

(21) International Application Number:
PCT/KR2005/000027

(22) International Filing Date: 6 January 2005 (06.01.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2004-0006029 30 January 2004 (30.01.2004) KR

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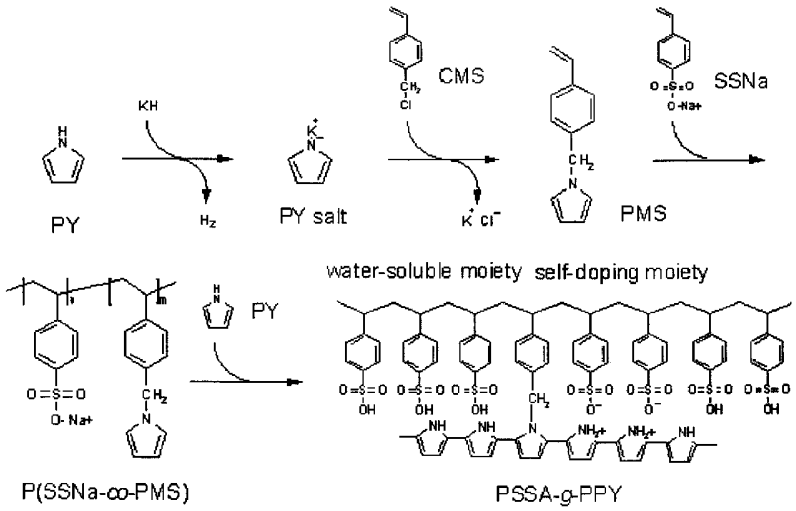
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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: A WATER-SOLUBLE AND SELF-DOPED CONDUCTING POLYPYRROLE GRAFT COPOLYMER



(57) Abstract: The present invention relates to a method for preparing a self-doped aqueous polypyrrole copolymer and the polypyrrole copolymer prepared by the same. The method for preparing the polypyrrole comprising the steps of: preparing a pyrrole salt by reacting pyrrole with potassium hydride (KH); preparing a pyrrolylmethylstyrene (PMS) by reacting said pyrrole salt with chloromethyl styrene (CMS); preparing a copolymer P(SSNa-co-PMS) by additive-polymerizing said pyrrolylmethyl styrene with sodium styrene sulfonate; and reacting said copolymer with pyrrole.

WO 2005/073262 A1

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Description

A WATER-SOLUBLE AND SELF-DOPED CONDUCTING POLYPYRROLE GRAFT COPOLYMER

Technical Field

[1] The present invention relates to a method for preparing a self-doped aqueous polypyrrole copolymer. Specifically the present invetion relates to a method for preparing the polypyrrole comprising the steps of: preparing a pyrrole salt by reacting pyrrole with potassium hydride (KH); preparing a pyrrolylmethylstyrene (PMS) by reacting said pyrrole salt with chloromethyl styrene (CMS); preparing a copolymer P(SSNa-co-PMS) by additive-polymerizing said pyrrolylmethyl styrene with sodium styrene sulfonate; and reacting said copolymer with pyrrole.

Background Art

[2] Polypyrrole is essentially one of conducting polymers which have been studying with the most activity. polypyrrole has been made conducting by proton-doping or oxidation-doping. It is well known that polypyrrole can be combined with high probability from comparatively cheap monomer, and it has excellent chemical stability and comparatively high conduction in view of conduction form [MacDiarmid, A.G. In Conjugated polymers and Related Materials, The Interconnection of Chemical and Electronic Structure; Salaneck, W.R.; Lundstrom, I.; Ranby, B., Eds.; Oxford University Press, 1993, PP 73-98].

[3] Polypyrrole may be used for application to secondary battery, electro-emitting element, electro chromic element and sensor owing to the excellent electric, electric-chemical and optical properties. Because polypyrrole used in the above applications should be prepared as film or coated shape, a method for preparing polypyrrole having self-doped property and capable of being manufactured from a solution may be highly required. But the production from a solution is very difficult in known manner because polypyrrole has backbone with stiff structure and the interaction between the chains of polymer.

[4] Polypyrrole may be prepared in organic solvent or aqueous solution by electro-chemical polymerization or chemical polymerization. When pyrrole is oxidation-polymerized by chemical method, an oxidation agent such as ferric chloride, ferric perchlorate and ammonium peroxydisulfate may be used. An additive to the reaction compound or the condition of polymerization may affect the properties of polymer greatly. A stable polypyrrole particle in colloidal state may be prepared with a polymer

stabilizer or surfactant [C.DeArmitt, S,.P. Armes, Langmuir 9 (1993) 652]. A process for forming a polypyrrole film on the surface of electrodes was studied in electro-chemical polymerization of pyrrole under the existence of sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (DBSNa) [S.Panero, P.Prosperi, B. Scrosati, Electrochem. Acta 37, 1992; 419].

[5] It has been reported by Kudoh that polypyrrole is polymerized using ferric sulfate as oxidation agent and DBSNa, sodium-n-alkyl-naphthalene-sulfonate and sodium-n-alkyl sulfate as anion surfactant [Y.Kudoh, Synth. Met. 79, 1996;17].

[6] It has been also reported that pyrrole is oxidation-polymerized under the existence of methylcellulose, poly(ethylene glycol), PVP, poly(acrylamide), poly(ethylene glycol). But unnecessary colloidal solution of polypyrrole may be obtained if the above neutral polymer is used. Recently, a method was suggested that pyrrole be oxidation-polymerized in matrix using cerium (IV) as oxidation agent [A.S. Sarac, B.Ustamehmetoglu, M.I.Mustafaev, C. Erbil, and G. Yzelli, J. Polym. Sci., Par A: Polym. Chem.,33, 1581, (1995)]. The oxidation-polymerization of polyaniline under polymer had been performed before the above report.

[7] Recent studies have been most interested in the preparation of the solution-processing polypyrrole, but the polypyrrole according to the method has disadvantage that the mechanical property is degraded in conducting circumstance. In this regard it is the greatest issue that the formulation of a composite or synthesis of a conducting copolymer is possible in view of application of conducting polymer. Many study organization has developed the formulation of a conducting polymer composite to result in improvement of mechanical or physical property. But in most conducting polymer the conductivity decreases eventually owing to aging property such as the escape of dopant with the passage of time. It may be suggested alternatively that the formulation of copolymer may avoid the aging phenomenon by chemical bond between matrix and conducting polymer.

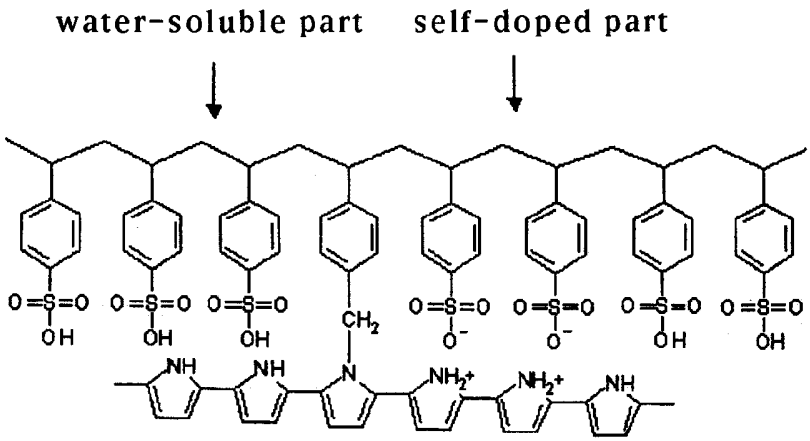
[8] For solving the problems with the prior inventions the development of polypyrrole composite with excellent electro-chemical property has been required in which the polypyrrole can be self-doped without imparting through proton-doping or oxidation-doping and can be processed in aqueous solution.

[9] The present invention provides a novel self-doped aqueous polypyrrole graft copolymer as structural formula 1 in the following and a method for preparing the same.

[10]

[11] [Structural formula 1]

[12]



[13]

Disclosure of Invention

[14]

[15] In a preferred embodiment of the present invention, there is provided with a novel polypyrrole graft copolymer.

[16] In other preferred embodiment, the number of repeat unit in polypyrrole graft copolymer of the present invention may be 2 to 400, and preferably 4 to 32. If the number of repeat unit is less than 2, then the conductivity is insignificant while if more than 400, the polymerization is impossible.

[17] In another preferred embodiment, polypyrrole graft copolymer of the present invention may be self-doped and water-soluble.

[18] In a further preferred embodiment, polypyrrole graft copolymer of the present invention may have the conductivity of 1.0×10 S/cm to 1.2×10^{-4} S/cm using four-probe method without the treatment of proton-doping or oxidation-doping.

[19] In a further preferred embodiment, there is provided with a method for preparing a polypyrrole graft copolymer comprising the following structural formula (1), comprising the steps of:

[20] preparing a pyrrole salt by reacting pyrrole with potassium hydride (KH);

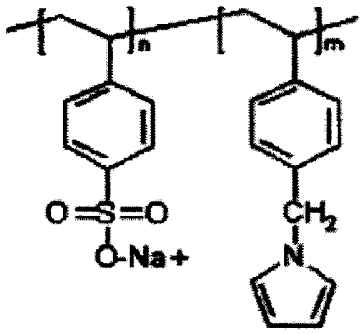
[21] preparing a pyrrolylmethylstyrene (PMS) by reacting said pyrrole salt with chloromethyl styrene (CMS);

[22] preparing a copolymer P(SSNa-co-PMS) comprising the following structural formula (2) by additive-polymerizing said pyrrolylmethyl styrene with sodium styrene sulfonate; and

[23] reacting said copolymer with pyrrole.

[24] [Structure formula 2]

[25]



P(SSNa-co-PMS)

[26] (wherein n = 1 to 500, and m = 1 to 1000)

[27]

[28] In a further preferred embodiment, the present invention provides a method for preparing polypyrrole graft copolymer, comprising the steps of:

[29] preparing pyrrole salt by reacting pyrrole (PY) with potassium hydride (KH), which is shown as reaction equation 1;

[30] preparing pyrrolylmethyl styrene (PMS) by reacting said pyrrol salt with chrolomethyl styrene (CMS), which is shown as reaction equation 2;

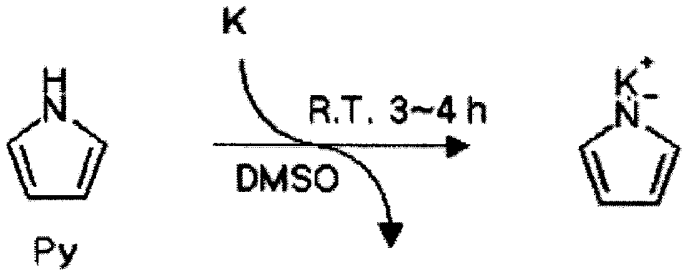
[31] preparing copolymer P(SSNa-co-PMS) of said pyrrolylmethyl (PMS) and sodium styrene sulfonate, which is shown as reaction equation 3;

[32] a self doped water-solube conducting polypyrrole graft copolymer by reacting said copolymer P(SSNa-co-PMS) with pyrrole, which is shown as reaction equation 4.

[33]

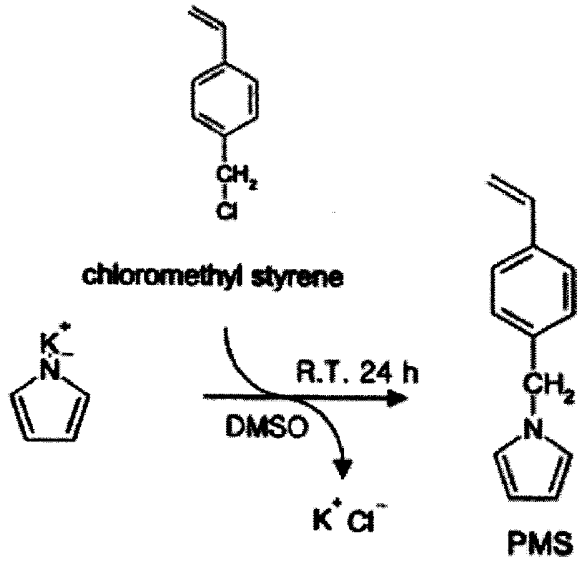
[34] [Reaction equation 1]

[35]



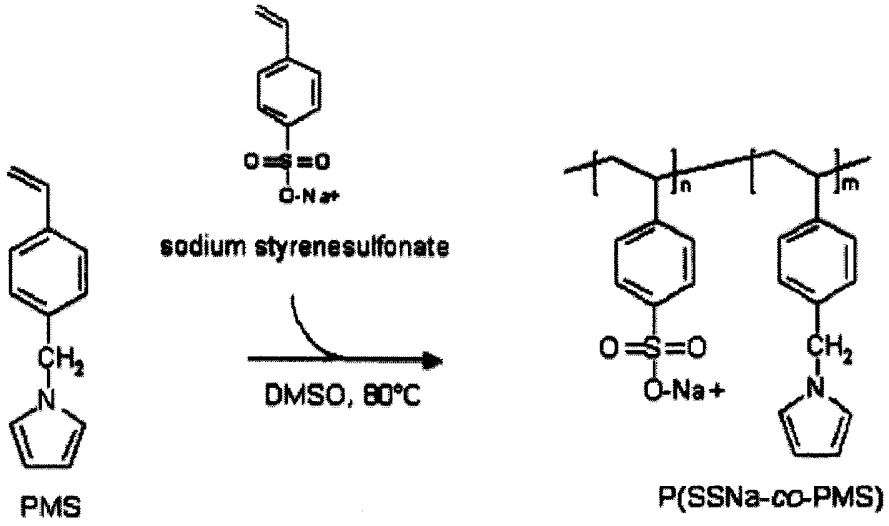
[36] [Reaction equation 2]

[37]



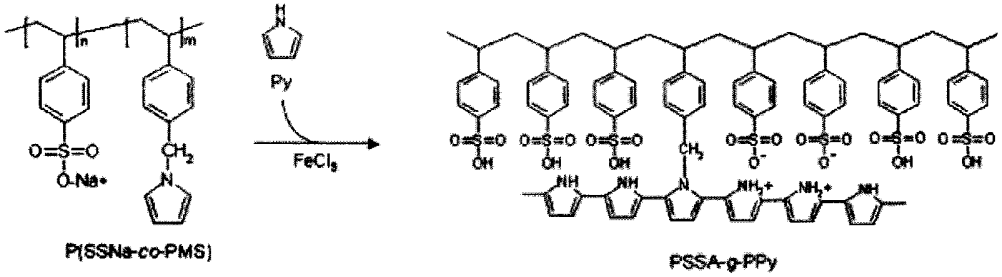
[38] [Reaction equation 3]

[39]



[40] [Reaction equation 4]

[41]



[42] All the process for preparing the polypyrrole graft copolymer is shown in figure 1.

[43]

Brief Description of the Drawings

[44] Figure 1 shows all the process for preparing the polypyrrole graft copolymer.

[45] Figure 2 shows synthetic route for PSSA-*g*-PPY. PY = pyrrole, CMS= chloromethyl styrene, PMS = pyrrolylmethyl styrene, SSNa = sodium styrene-sulfonate, P(SSNa-*co*-PMS) = poly(sodium styrenesulfonate-*co*-pyrrolyl- methyl styrene).

[46] Figure 3 shows ^{1}H NMR spectra of (a) PMS in $CDCl_3$, (b) P(SSNa-*co*-PMS) in D_2O and (c) PSSA-*g*-PPY in $D_2O + H_2O$.

[47] Figure 4 shows UV-visible spectra of PSSA-*g*-PPY: (a) self-doped state in aqueous solution and (b) de-doped state in aqueous NH_4OH (1 *M*) solution.

[48] Figure 5 shows Illustration of the hydrodynamic volume and structural change of PSSA-*g*-PPY (a) in water and (b) in aqueous NH4OH (1 *M*) solution.

[49] Figure 6 shows the XRD pattern of (a) PSSA-g-PPY and (b) P (SSNa-co-PMS).

[50]

Mode for the Invention

[51] The method for preparing pyrrolylmethylstyrene will be described more specifically in the following.

[52] After n-hexane was filled as suitable amount into three-neck flask, potassium hydride (KH) in mineral oil puts into the flask. n-hexane and the oil were extracted with a syringe and the flask was filled with n-hexane again to extract repeatedly for washing, and then the flask was dried. Pyrrole (PY) was added into the flask and at same time the mixture was stirred after Tetra hydro-furan (THF) was added into the flask. After stirring was continued for 1 to 20 hour at room temperature, chloro-methyl styrene (CMS) is added ant reaction is sustained about 1 to 20 hours. The reaction solution was conveyed to a separatory funnel, and then only the organic phase was separated after the addition of ether and water. With similarity resultant organic phase was removed after washing many times with the addition of only water, and then remaining water was removed using the addition of suitable $MgSO_4$. The final organic solvent was evaporated in vacuum after filtering with filter-paper. For separating only PMS which reacted with pyrrole from the resultant, the column chromatography was used for obtaining the final product (the yield rate = 50 to 95 %). The column in the chromatography was n-hexane.

[53]

[54] A method for preparing the copolymer of said pyrrolylmethyl styrene (PMS) and sodium styrene sulfonate (SSNa) will be described more specifically in the following.

[55] P(SSNa-co-PMS) was synthesized by radical copolymerization of SSNa and PMS. SSNa and BOC-AMS was dissolved into dimethyl sulfoxide (DMSO), and then AIBN was added as an initiator to be stirred for 1 to 30 hours at 50 to 100 ℃. The resultant solution was precipitated into acetone. The obtained copolymer was washed several times with acetone and then dried in vacuum. And also the structure of the copolymer was analyzed with FT-IR and ^{1}H NMR.

[56]

[57] PSSA-g-PPY according to the present invention will be described more specifically in the following.

[58] PSSA-g-PPY was prepared by graft-reacting pyrrole with said copolymer P(SSNa-co-PMS).

[59] For pyrrole-graft-reaction the temperature was lowered, and pyrrole was dissolved into HCl solution to polymerize using ammonium sulfate as oxidation agent. In such case, the equivalent of the oxidation agent and pyrrole was adjusted as 1: 1. A dark solution was obtained after reacting for 1 to 20 hours. The obtained solution was further purified by dialysis using a membrane with 3000 molecular weight cutoff. The distilled water out of the membrane was exchanged several times until pH increase no longer for some days. Finally, the purified solution was precipitated into acetone, and then dried in vacuum.

[60] The obtained PSSA-g-PPY was experimented with FT-IR and ^{1}H NMR for analyzing the structure, which is shown in Figure 3 and 4.

[61]

[62] As shown in Figure 3, comparing (a) with (b), the characteristic peak of PMS in the FT-IR spectrum of P(SSNa-co-PMS) was shown in 1629, 1565 and 486 cm^{-1}, respectively, which is different from that of PSSNa. This verifies that the copolymerization of PMS and SSNa was successful. And also, as shown in Figure 3 (c), regarding to PSSA-g-PPY it is noted that the characteristic peak of pyrrole was more peculiar. This confirms qualitatively that P(SSNa-co-PMS) and pyrrole was successfully graft-copolymerized. And also ^{1}H NMR spectrum shown in Figure 4 verifies the structure depicted schematically in Figure 2.

[63] For comparison of PSSA-g-PPY, PSSA/PPY blend was prepared and the difference of characteristics was shown. The preparation of PSSA/PPY blend was similar to the

PSSA-g-PANI, except for using PSSNa as primary chain instead of P(SSNa-co-PMS). PSSA-g-PPY remained in the completely dissolved state in aqueous solution or am monium solution (1M), but the blend remained in the diffused state in ammonium solution to finally be precipitated as de-doping caused conglomeration together. The result is shown in Figure 2. In case of graft copolymer, even though the de-doping occurs, the macro-separation of polypyrrole cannot happen owing to the chemical bonding. Further if the ammonium solution is removed, PSSA-g-PPY was recovered from violet to the original dark green as result of re-doping, the phenomenon such as doping to de-doping and vice versa occurred reversibly depending on pH without external dopant.

[64] For the measurement of conductivity a powder sample was pressurized by press to form pellet and the conductivity of the pellet was measured suing four-probe method. The conductivities of PSSA-g-PPY and PSSA/PPY blend at room temperature were 4.8×10^{-1} S/cm and 9.5×10^{-2} S/cm, respectively, which show the difference of conductivity.

[65] UV-Vis spectrum of PSSA-g-PPY is shown in Figure 5.

[66] When PSSA-g-PPY was dissolved into aqueous solution, absorption peaks owing to polaron band shift were observed in 383 nm and 492 nm. The wave-lengths of the peaks are characteristic of that of doping polypyrrole, which shows directly that PSSA-g-PPY was self-doped. Further, if PSSA-g-PPy was dissolved into ammonium solution, the peak in the state of conductivity disappeared, which shows that de-doping occurred in ammonium solution.

[67] The conductivity of PSSA-g-PPY was slightly larger than that of PSSA-g-PANI grafted with aniline (refer to Korea patent application no. 10-2003-0051225). If equal amount of conducting polymers are prepared as identical process, the conductivity of polypyrrole is better than that of polyaniline, which provides a clue to compare graft-copolymer. Further the conductivity difference was not caused from the conformation difference, which can be conformed from the fact that PSSA-g-PPY has not a definite form and the conductivity is not affected with crystallization as shown in Figure 6.

[68] After PSSA-g-PPY was dried in high vacuum above 24 hours for removing the remaining moisture, PSSA-g-PPY was dissolved completely into water and DMSO, and as result Tyndall phenomenon was not observed.

[69]

[70] The present invention will be described in detail with examples, not limiting the present invention.

[71]

[72] Example 1

[73] Synthesis of water-soluble self-doped polypyrrole graft copolymer (Variation with molecular weight of backbone)

[74] Sodium styrene sulfonate 5.0 g and PMS 0.5 g was dissolved into DMSO 60 ml, and then the solution was stirred using AIBN 0.01 to 0.2 g as an initiator for 15 hours at 80 ℃. The obtained solution was precipitated into over-excessive amount of acetone. The obtained copolymer was washed several times with acetone, and then dried in vacuum for 24 hours at 60 ℃. The copolymer was analyzed using High resolution Maldi Tof Mass spectrometer, which showed that the copolymer is random copolymer with 500 to 100,000s of molecular weight.

[75]

[76] Example 2

[77] Synthesis of graft copolymer (Variation of the graft length)

[78] Sodium styrene sulfonate 5.0 g and PMS 0.5 g was dissolved into DMSO 60 ml, and then the solution was stirred using AIBN 0.1 g as an initiator for 15 hours at 80 ℃. The obtained solution was precipitated into over-excessive amount of acetone. The obtained copolymer was washed several times with acetone, and then dried in vacuum for 24 hours at 60 ℃. For pyrrole graft reaction, the temperature was lowered to 0 ℃, and the amount of pyrrole + P(SSNa-co-PMS) was adjusted as 1 g and was dissolved into aqueous solution 30 ml to polymerize using ammonium sulfate as oxidation agent. In such case, the equivalent of oxidation agent and pyrrole was adjusted as 1: 1.

[79] In the obtained graft copolymer the average number of pyrrole repeat units varied 2 to 100 depending on the condition of the experiment, and if the number of pyrrole repeat units was more than 20, the graft copolymer was insoluble in water. The larger is the number of pyrrole repeat units, the smaller is the number of sulfonic acid group participating in reaction to degrade the solubility.

[80]

[81] Example 3

[82] Synthesis of water-soluble self doped pyrrole graft copolymer (the density variation of graft site)

[83] Sodium styrene sulfonate 5.0 g and PMS 0.05 g to 0.2 g was dissolved into DMSO 60 ml, and then the solution was stirred using AIBN 0.1 g as an initiator for 15 hours at 80 ℃. The obtained solution was precipitated into over-excessive amount of acetone. The obtained copolymer was washed several times with acetone, and then dried in

vacuum for 24 hours at 60 ℃. The obtained copolymer was analyzed by ^1H NMR, and the result showed that the contents of PMS in reactant were nearly consistent with that of PMS in product (copolymer).

[84]

[85] Example 4

[86] Synthesis of water-soluble self-doped polypyrrole graft copolymer (the variation of pH)

[87] For pyrrole graft reaction, the temperature was lowered to 0 ℃, and 0.1 g pyrrole was dissolved into 50 ml HCl solution containing 1.0 g P(SSNa-co-PMS) for 30 minutes to polymerize using 0.33 g ammonium sulfate as oxidation agent. The concentrate of HCl solution varied 0.1 to 2.0 M in this experiment. The equivalent of oxidation and pyrrole was adjusted as 1: 1. After reaction for 6 hours the dark solution was obtained.

[88]

[89] Example 5

[90] A water-soluble self-doped polypyrrole graft copolymer P(SSNa-co-PMS) by electro-chemical polymerization was dissolved into water as amount of 1 to 10 wt%, and then water was evaporated by spin-coating method on platinum electrodes or vacuum dry method. Platinum electrode coated with P(SSNa-co-PMS) was swollen more than 1 hour within a electro-chemical copolymerization device using the mixture solution of 1 M HCl solution or 1 M $LiClO_4$ solution, and DMF or acetonitrile as solvent. Dried nitrogen was substituted for within the device for 30 minute to 2 hours to polymerize electro-chemically. The working electrode was platinum electrode coated with P(SSNa-co-PMS), and base electrode was standard calomel electrode, and the relative electrode was platinum wire. The polymerization was performed for 30 minutes to 2 hours circulating -0.2 to 1.0 V with circulation current/voltage. After polymerization, the platinum electrode was dried in vacuum at room temperature for 24 hours, and then PSSA-g-PPY sample coated on surface was obtained independently.

[91]

Industrial Applicability

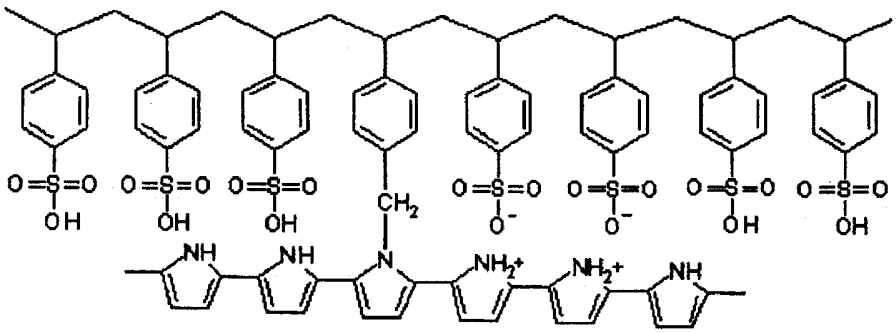
[92] The self-doped water-soluble polypyrrole according to the present invention has advantage that the backbone itself acts on dopant and at the same time has the function of solubility. And also it has advantage that the macro-phase separation of polypyrrole to each other can be avoided owing to the branch of the backbone, and doping and de-

doping may occur with reversibility depending on pH. The self-doped water-soluble polypyrrole according to the present invention may be used for materials shielding EMI, anti-electrification, anti-corrosion, electrodes for secondary battery, electro-chromic material and functional film.

Claims

[1] 1. A polypyrrole graft copolymer comprising the following structural formula (1):

[Structural formula 1]



[2] 2. The polypyrrole graft copolymer according to claim 1, wherein the number of pyrrole repeat units is 2 to 400.

[3] 3. The polypyrrole graft copolymer according to claim 1, wherein the number of pyrrole repeat units is 4 to 32.

[4] 4. The polypyrrole according to any one of claim 1 to 3, wherein the polypyrrole graft- copolymer is self-doped and water-soluble.

[5] 5. The polypyrrole according to any one of claim 1 to 3, wherein the conductivity is 1.0×10 S/cm to 1.2×10^{-4} S/cm in 4-termianl method without the treatment of proton or oxidation doping.

[6] 6. A method for preparing a polypyrrole graft copolymer comprising the following structural formula (1), comprising the steps of:

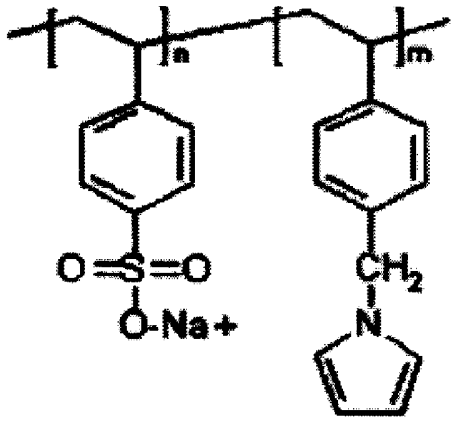
preparing a pyrrole salt by reacting pyrrole with potassium hydride (KH);

preparing a pyrrolylmethylstyrene (PMS) by reacting said pyrrole salt with chloromethyl styrene (CMS);

preparing a copolymer P(SSNa-co-PMS) comprising the following structural formula (2) by additive-polymerizing said pyrrolylmethyl styrene with sodium styrene sulfonate; and

reacting said copolymer with pyrrole.

[Structural formula 2]



P(SSNa-co-PMS)

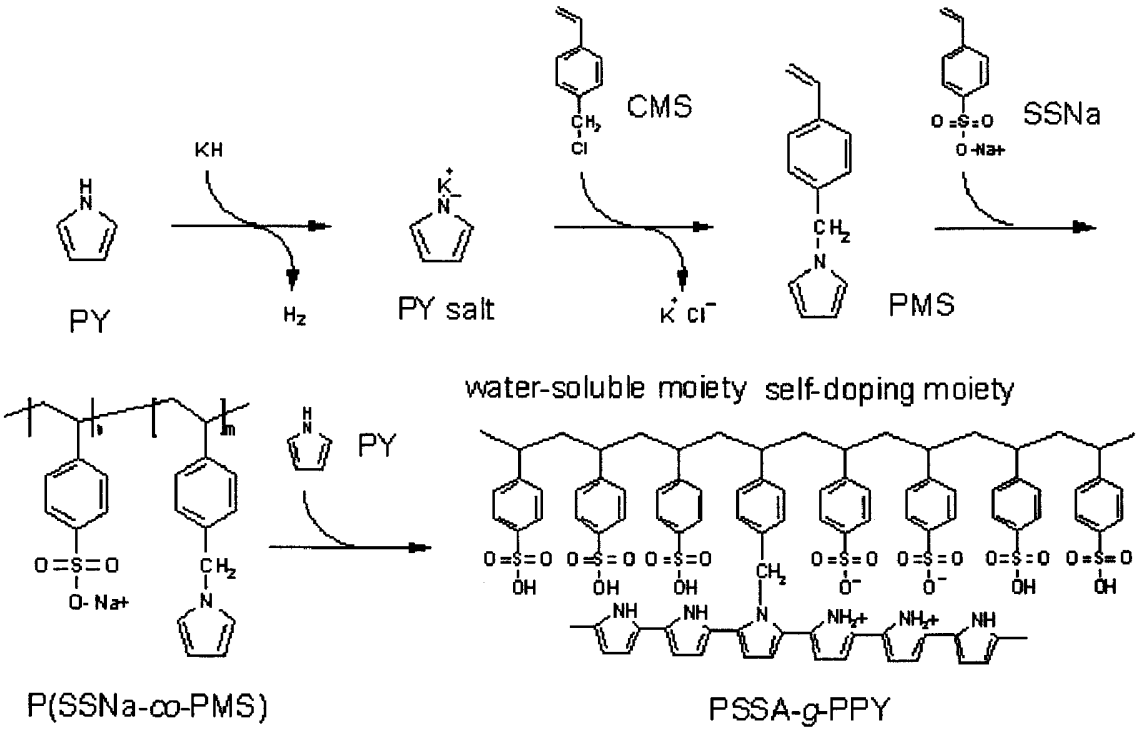
(wherein n = 1 to 500, and m = 1 to 1000)

[7] 7. The method according to claim 6, wherein the reaction of said pyrrolyl methyl styrene (PMS) and said sodium styrene sulfonate comprises electro-chemical graft-polymerization.

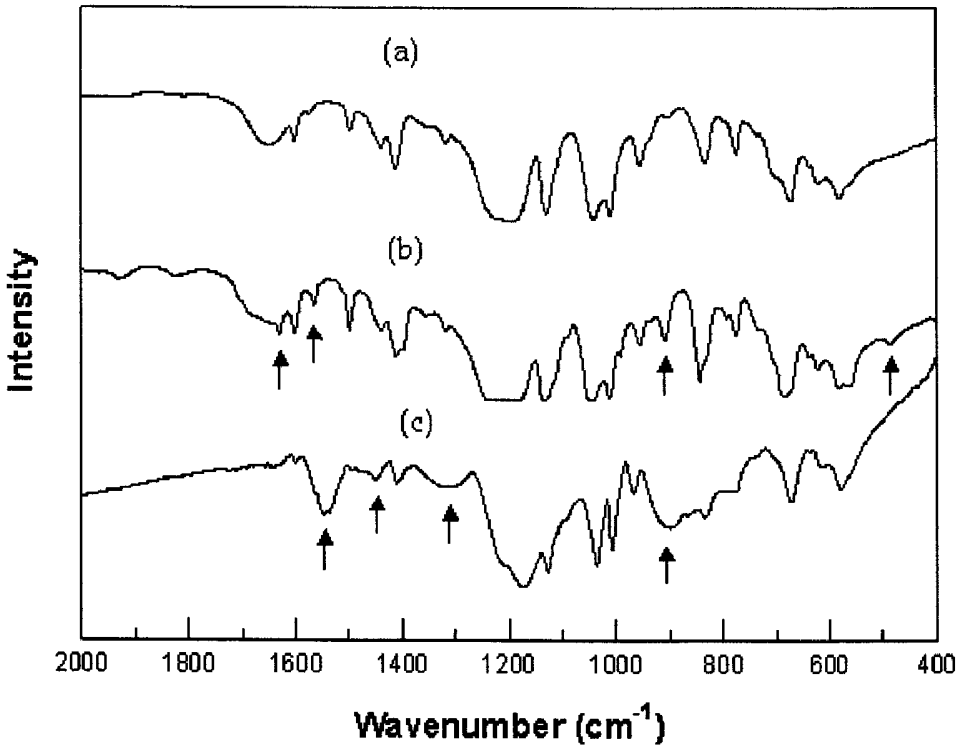
[8] 8.The method according to claim 7, wherein in said electro-chemical working electrode is platinum electrode coated with sodium styrenesulfonate copolymer P(SSNa-co-PMS), base electrode is standard calomel electrode, and relative electrode is platinum wire.

[9] 9 A material comprising the polypyrrole graft copolymer according to claim 1.

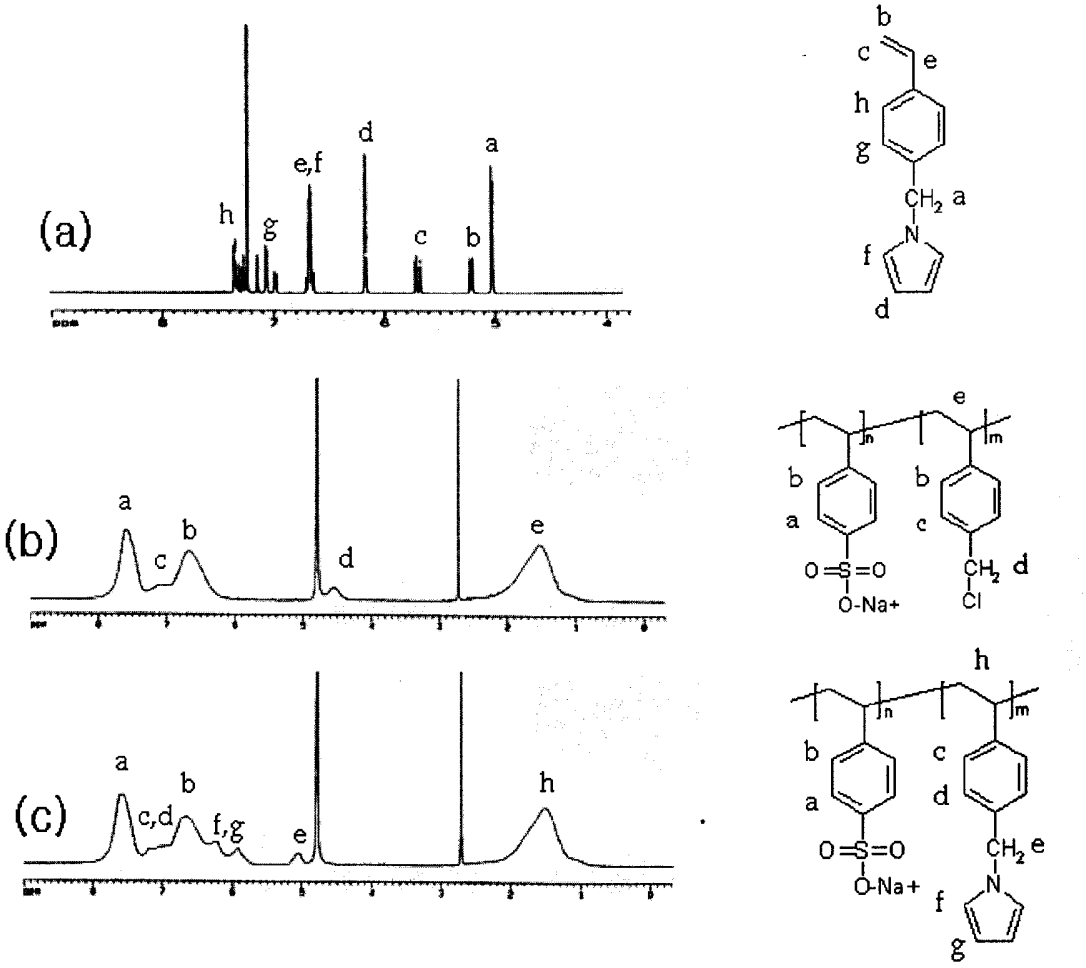
[Fig. 1]


KH
PY
H2
PY salt
CMS
K+ Cl-
PMS
SSNa
water-soluble moiety self-doping moiety
PY
P(SSNa-co-PMS)
PSSA-g-PPY

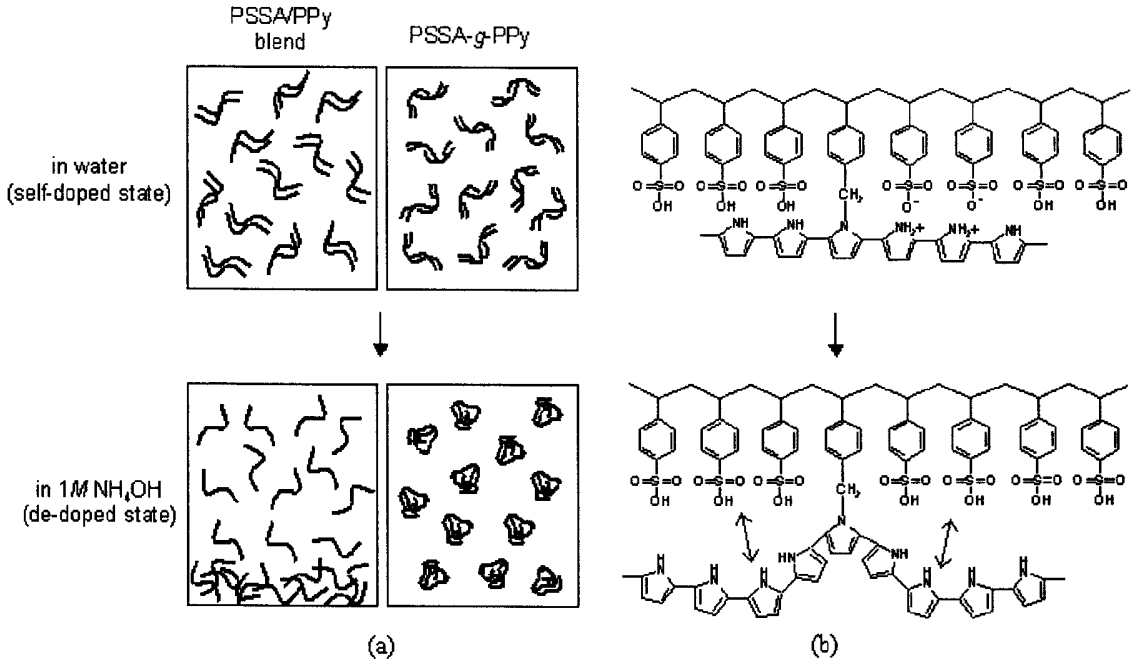
[Fig. 2]


(a)
(b)
(c)
Intensity
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm-1)

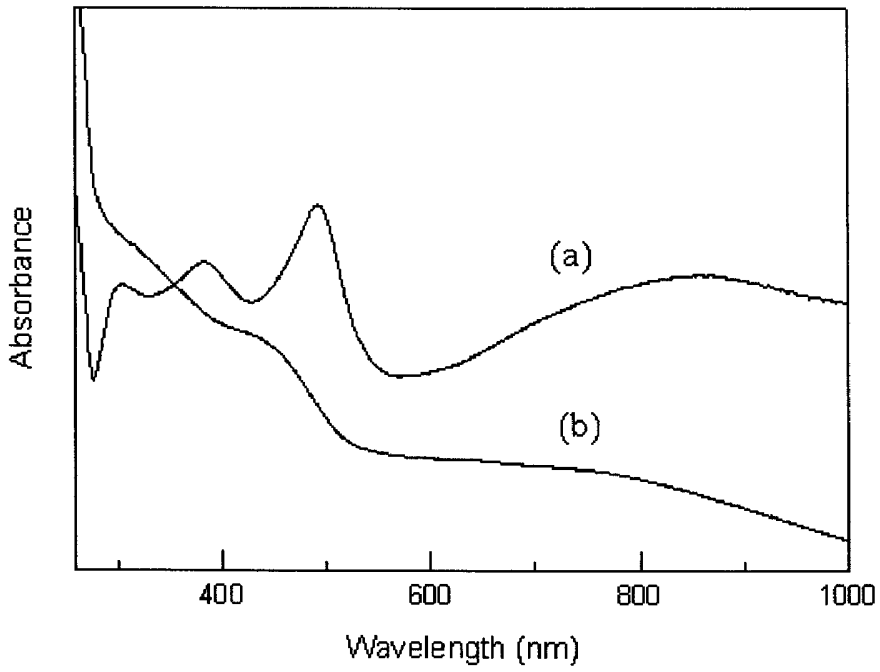
[Fig. 3]


(a)
h
g
e,f
d
c
b
a
(b)
a
c
b
d
e
(c)
a
c,d
b
f,g
e
h
b
c
e
h
a
d
f
g
O-Na+
Cl

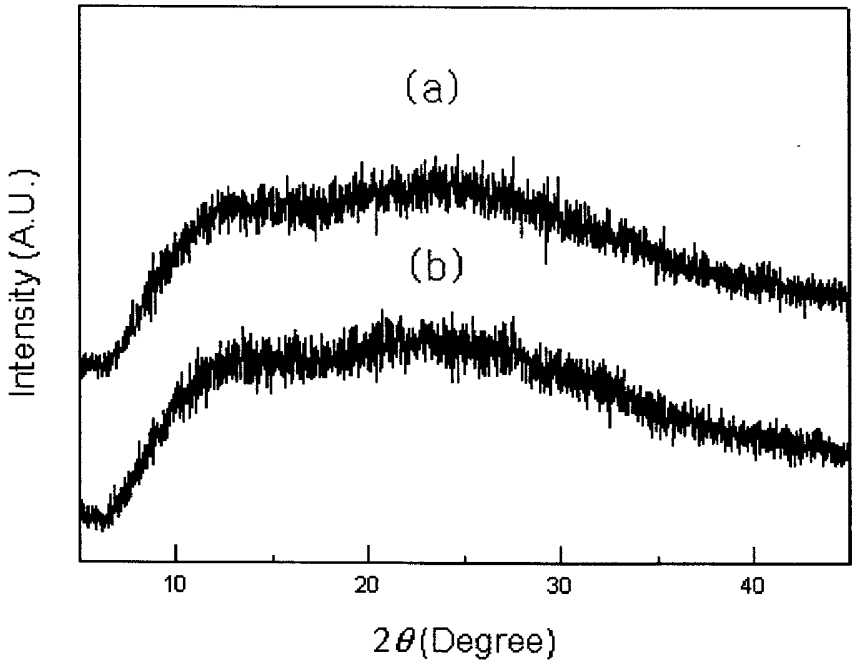
[Fig. 4]


PSSA/PPy blend
PSSA-g-PPy
in water (self-doped state)
in 1M NH4OH (de-doped state)
(a)
(b)

[Fig. 5]


Absorbance
(a)
(b)
400
600
800
1000
Wavelength (nm)

[Fig. 6]


Intensity (A.U.)
(a)
(b)
10
20
30
40
2θ(Degree)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/000027

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08F 271/02

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)
IPC7 C08F 271/02, C08G 73/02, B32B 5/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and Applications for Invention since 1975
Korean Utility models and Applications for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
KIPASS, PAJ, Wiley Inter Science

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, E	Woo Jin Bae et al., 'A water-soluble and self-doped conducting polypyrrole graft copolymer', Macromolecules, 2005, vol.38, p1044-1047 (published on web 21 January 2005) see the whole document	1-9
X, P	Woo Jin Bae et al., 'Synthesis and Characterization of water-soluble and self-doped conducting polypyrrole graft copolymer', Proceeding of the Polymer Society of Korea(Spring), 2004, Vol.29, No.1, p381 (published on 09 April 2004) see the whole document	1-9
Y	Woo Jin Bae et al., 'A novel water-soluble and self-doped conducting polyaniline graft copolymer', Chem. Commun., 2003, p2768-2769 (published on the web 09 October 2003) see the whole document	1-9
Y	Yun Heum Park et al., 'Preparation and characterization of conducting poly(acryloyl chloride)-g-polypyrrole copolymer', Polymer. Adv. Technol., 2002, Vol. 13, p670-677 see the whole document	1-9
A	Woo Jin Bae et al., 'Preparation of polystyrene/polyaniline blends by in situ polymerization technique and their morphology and electrial property', Synthetic Metals, 2003, Vol. 132, p239-244. see the whole document	1-9

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

☒ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 APRIL 2005 (18.04.2005)	**20 APRIL 2005 (20.04.2005)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	BAHN, Yong Byung Telephone No. 82-42-481-5539

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/000027

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 07-233244 A (Showa Denko KK) 05 September 1995 see the whole document	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2005/000027

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		FR 2718140 A1	06.10.1995
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