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(54) **Title**: SYNTHESIS OF DIOXYHETEROCYCLE-BASED POLYMERS

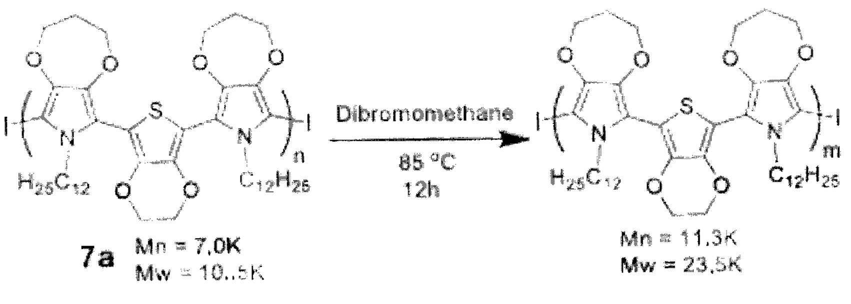

Figure 6

(57) **Abstract**: A method of polymerization for the preparation of conjugated polymers and copolymers comprising dioxypyrrole and/or dioxyfuran repeating units involves the halogen, JV-haloimide, or N-haloamine promoted polymerization of monomers and/or oligomers comprising one or more dioxypyrrole and/or dioxyfuran units. The polymerization can be carried out over a wide range of temperatures and can be carried out with or without a solvent. The monomers allow the preparation of polymers having an oligomeric repeating unit comprising a conjugated unit other than a dioxypyrrole or dioxyfuran that is bound to two dioxypyrrole or dioxyfuran units.

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DESCRIPTION

SYNTHESIS OF DIOXYHETEROCYCLE-BASED POLYMERS

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims the benefit of U.S. Provisional Application Serial No. 61/597,949, filed February 13, 2012, which is hereby incorporated by reference herein in its entirety, including any figures, tables, or drawings.

BACKGROUND OF INVENTION

Conjugated conducting polymers displaying moderate charge mobilities, an ability to be redox doped to highly conducting compositions, and an ability to change optical properties reversibly, can be used as color changing materials, conductors, and antistatic coatings in electronic components, photovoltaic devices, and light emitting devices. One class of conducting polymers, polyheterocycles, which include polythiophenes, polypyrroles, and polyfurans, have been developed for their use in electrochromic devices, photovoltaic devices, and light emitting diodes. Appending a 3,4-alkylenedioxy bridge on the heterocycle allows a modified polyheterocycle, where the bridge does not cause an undesirable conformational change in the backbone of the polymer, and the electron donating effect of the oxygen substituents increases the HOMO of the conjugated polymer, reducing both its oxidation potential and its electronic band gap. Poly(3,4-dioxythiophene)s have been extensively studied, poly(3,4-dioxypyrrole)s are somewhat less well known, and poly(3,4-dioxyfuran)s are not well documented.

Poly(3,4-dioxypyrrole)s are materials that display high electronic band gaps and low oxidation potentials, and have properties that make them excellent candidates as sensors, supercapacitors, and electrochromic devices where high conductivity and processability are needed. The syntheses and properties of a wide variety of poly(3,4-dioxypyrrole)s have been reported, for example, in: Walczak *et al.*, *Adv. Mater.* **2006**, *18*, 1121-31; Schottland *et al.*, *Macromolecules* **2000**, *33*, 7051-61; Sonmez *et al.*, *Macromolecules* **2003**, *36*, 639-47; Thomas *et al.*, *Adv. Mater.* **2000**, *12*, 222-5; and Walczak *et al.*, *Macromolecules* **2007**, *40*, 7777-85.

More recently, the polymerization of 2,5-diodo-3,4-alkylenedioxypyrrole in bulk or using a suitable solvent has been disclosed in Reynolds *et al.*, US Patent No. 7,649,076 and

Walczak *et al.*, *Macromolecules* **2008**, *41*, 691-700. By this method, high molecular weight polymer can be prepared without the use of metals, oxidants, solvents, or other additives. Additionally, reaction can be carried out in aqueous solution and tolerates substitution by a wide variety of functionalities, including those that cannot be synthesized by an oxidative polymerization process. This polymerization, as shown in Scheme 1, requires a three-step synthesis that starts from a 3,4-dioxypyrrole-2,5-diacid and requires isolation and purification of the intermediate 2,5-di-iodo-3,4-dioxypyrrole monomer. However, the isolation and purification steps reduce overall yield and throughput. Furthermore, the polymerization process is limited to the types of 3,4-dioxypyrrole monomers reported in Reynolds *et al.* Hence, a method that does not require the use of 2,5-di-iodo-3,4-dioxypyrrole and can expand the range of 3,4-dioxypyrrole-based monomers that can be polymerized efficiently is desirable.

BRIEF SUMMARY

Embodiments of the invention are directed to conjugated polymers and methods of their preparation. Conjugated polymers have a multiplicity of 3,4-dialkoy of 3,4-alkylenedioxy pyrrole or furan repeating units. The polymers can also include additional conjugated repeating units that are isolated by 3,4-dialkoy of 3,4-alkylenedioxy pyrrole or furan repeating units. The additional conjugated repeating units include 1,2-ethenediyl, 1,4-butadienediyl, 1,4-benzenediyl, 2,6-naphthalendiyl, 9,10-anthracenediyl, 2,7-fluorenediyl, 2,5-furandiyl, 2,5-thiophenediyl, 2,5-pyrroldiyl, 2,1,3-benzothiadiazole-4,7-diyl, 2,7-carbazolediyl, 2,6-pyridinediyl, 1,4-bis(2',2''-thiophenyl)benzene-5',5''-diyl, and/or 4,7-*bis*-(2',2''thiophenyl)-2,1,3-benzothiadiazole-5',5''-diyl units. In embodiments of the invention, the end-groups of the conjugated polymers can be a halogen, hydrogen or C(O)OR^7, where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium. In other embodiments of the invention, the end-groups can have selected functionality.

According to an embodiment of the invention, one or more monomers and/or oligomer that includes a terminal 3,4-dialkoy of 3,4-alkylenedioxy pyrrole or furan substituted at a 2- and/or 5- position with a H, chlorine, bromine, iodine, or C(O)OR^7, where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium, is polymerized or copolymerized upon addition of a halogen, *N*-haloimide or *N*-haloamine. Optionally, an acid can be included. Optionally the polymerization mixture can be irradiated with ultraviolet light. The polymerization can be carried out as the neat monomer(s) and/or oligomer(s) or a solvent can be included. Polymerizing or copolymerizing can be carried out over a wide range of temperatures and can be carried out under mild conditions, for example, 0 to 100 °C. End-capping 3,4-dialkoy of 3,4-alkylenedioxy pyrrole or furan monomers can be included, where one substituent is a 2- or 5- H, chlorine, bromine, iodine, or $C(O)OR^7$, where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium for incorporation into the polymer or copolymer and another functionality that is designed to provided an additional end-group that can be used to provide functionality for subsequent condensation, addition, or complexation with other monomers, oligomers, polymers, resins, surfaces, salts, or particles to form coupled polymers, block copolymers, multiblock copolymers, networks, aggregates, functionalized resins, functionalized surfaces, or functionalized particles.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows exemplary L groups for oligomeric monomers according to an embodiment of the invention.

Figure 2 shows a reaction scheme for the prior art preparation of a poly(3,4-dioxypyrrole) by a three-step process with the isolation of a 2,5-diiodo-3,4-dioxypyrrole.

Figure 3 shows a reaction scheme for the halodecarboxylation of a model 2-carboxylic acid 3,4-propylenedioxypyrrole and a model 2-*H* 3,4-propylenedioxypyrrole using *N*-halosuccinimides.

Figure 4 shows a reaction scheme for the iododecarboxylation of a model 2-potassiun carboxylate 3,4-propylenedioxypyrrole using iodine.

Figure 5 shows a reaction scheme for the *in situ* halodecarboxylation-dehalogenation polycondensation of **6** and **14** using various halogens or *N*-halosuccinimides, according to an embodiment of the invention.

Figure 6 shows a reaction scheme for the dehalogenation coupling of an α,ω-diiodo conjugated polymer, **7a**, to a higher molecular weight conjugated polymer, according to an embodiment of the invention.

Figure 7 shows a) electromagnetic absorption spectra for neutral and oxidized spray-cast films of α,ω-diiodo conjugated polymer, **7a**, on ITO-coated glass from DCM solution (2 mg/mL); and b) cyclic voltammograms of the **7a** where electrochemical oxidation of the film was carried out in $TBAPF_6$ [0.2M]/ACN using a Ag/Ag+ reference electrode and a platinum counter electrode.

Figure 8 shows a ^{1}H-NMR spectrum of **6a**.

Figure 9 shows a ^{13}C-NMR spectrum of **6a**.

Figure 10 shows a GPC chromatograph with tabulated data for polymer **7a**, according to an embodiment of the invention.

Figure 11 shows a ^{1}H-NMR spectrum of polymer **7a**, according to an embodiment of the invention.

Figure 12 shows a ^{13}C-NMR spectrum of polymer **7a**, according to an embodiment of the invention.

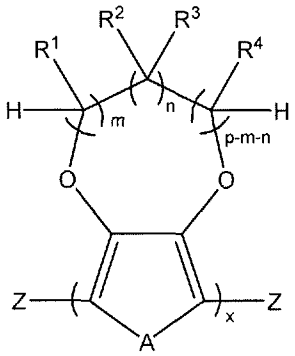
Figure 13 shows a GPC chromatograph with tabulated data for polymer **16a**, prepared according to an embodiment of the invention.

Figure 14 shows a ^{1}H-NMR spectrum of polymer **16a**, prepared according to an embodiment of the invention.

Figure 15 shows a ^{13}C-NMR spectrum of polymer **16a**, prepared according to an embodiment of the invention.

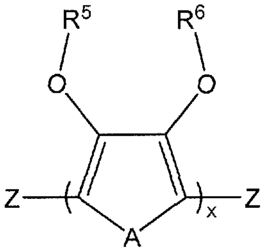
DETAILED DISCLOSURE

An embodiment of the invention is directed to a method for the preparation of a conjugated polymer, where the conjugated polymer is: a poly(dioxypyrrole), either a poly(3,4-dialkyloxypyrrole), poly(3,4-alkylenedioxypyrrole), or poly(3,4-alkylenedioxypyrrole-co-3,4-dialkyloxypyrrole); a poly(dioxyfuran), either a poly(3,4-dialkyloxyfuran), poly(3,4-alkylenedioxyfuran), or poly(3,4-alkylenedioxyfuran-co-3,4-dialkyloxyfuran); or a poly(dioxypyrrole-co-dioxyfuran), either a poly(3,4-alkylenedioxypyrrole-co-3,4-dialkyloxyfuran), a poly(3,4-alkylenedioxyfuran-co-3,4-dialkyloxypyrrole), a poly(3,4-alkylenedioxypyrrole-co-3,4-alkylenedioxyfuran), or poly(3,4-dialkyloxypyrrole-co-3,4-dialkyloxyfuran) via the halogen, *N*-haloimide, or *N*-haloamine promoted homopolymerization or copolymerization of monomers comprising 2,5-disubstituted-3,4-dialkyloxypyrrole, 2,5-disubstituted-3,4-alkylenedioxypyrrole, 2,5-disubstituted-3,4-dialkyloxyfuran, 2,5-disubstituted-3,4-alkylenedioxyfuran, any oligomers thereof, or any combination of monomers and oligomers thereof. In an embodiment of the invention, the polymerization involves halogen, *N*-haloimide, or *N*-haloamine promoted homopolymerization or copolymerization of: 2,5-disubstituted-3,4-alkylenedioxypyrrole and/or 2,5-disubstituted-3,4-alkylenedioxyfuran comprising monomers or oligomers of the structure:



(I)

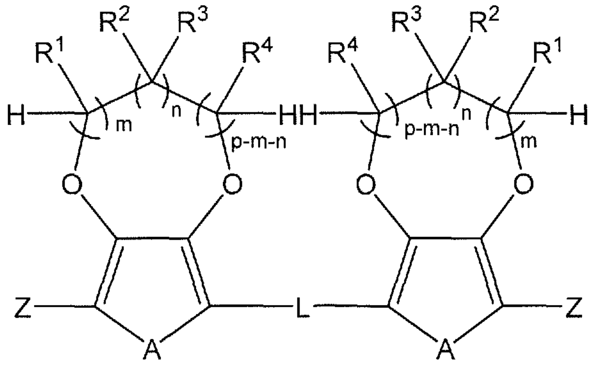
and/or 2,5-disubstituted-3,4-dialkyloxypyrrole and/or 2,5-disubstituted-3,4-dialkyloxyfuran monomers or oligomers of the structure,



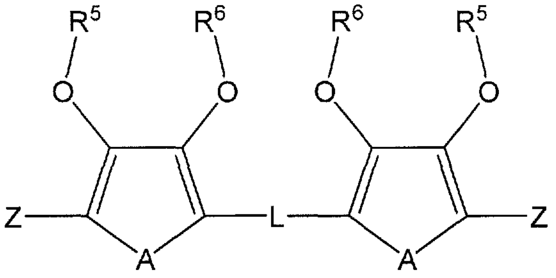
(II)

where: x is 1 to 10; R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; when x is 1, Z is H or $C(O)OR^7$, wherein R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium where 1 to 4 of the substituents on the ammonium N is H, C_1 to C_8 alkyl, aryl, or alkyl aryl groups; when x > 1, Z is H, chlorine, bromine, iodine, or $C(O)OR^7$; and A is O or NR, wherein R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X where X is $C(O)R^8$, CH_2YR^9, or $CR^{10}=CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, where Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$, and where R^9, R^{10}, R^{11}, R^{12}, R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl. The polymerization can be carried out over a wide range of temperatures, for example, about 20 to about 100 °C, and can be carried out in the presence of air or in an inert atmosphere. The polymerization can be carried out in a neat liquid phase, as an amorphous solid, in solution, for example, in dichloromethane (DCM), dibromomethane, or tetrahydrofuran (THF), or in an emulsion of an organic solvent and water. As desired or required, the polymerization mixture can be irradiated with UV radiation or include an acid, for example, a Lewis acid, for example, $FeCl_3$. The resulting homopolymers or copolymers have repeating units that are indicated between the parentheses of structures I and/or II and end-units that comprise chlorine, bromine, or iodine; depending on the halogen, *N*-haloimide, or *N*-haloamine, for example, *N*-halosuccinimide. To achieve high molecular weight homopolymers or copolymers, at least two equivalents of the halogen, *N*-haloimide, or *N*-haloamine per mole of monomer or oligomer I and/or II are required.

Another embodiment of the invention is directed to polymers comprising oligomeric bis-dioxypyrrole and/or bis-dioxyfuran repeating units in a homopolymer or copolymer, such that all L units are separated by two or more dioxypyrrole or dioxyfuran units. The oligomeric bis-dioxypyrrole or bis-dioxyfuran repeating units result from polymerization of reaction mixtures that include oligomers of the structures:



(III) or

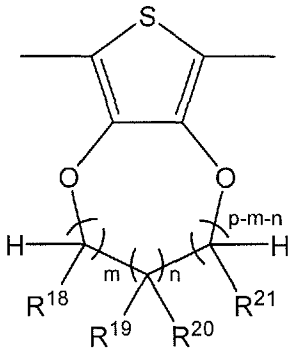


(IV),

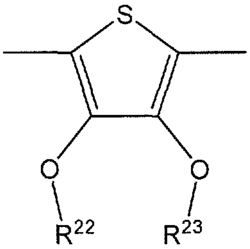
where: R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; Z is H, chlorine, bromine, iodine, or $C(O)OR^7$, wherein R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium, where 1 to 4 of the substituents on the ammonium is to H, C_1 to C_8 alkyl, aryl, or alkyl aryl groups; A is O or

NR, wherein R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X where X is $C(O)R^8$, CH_2YR^9, or $CR^{10}{=}CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, where Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$, and where R^9, R^{10}, R^{11}, R^{12}, R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl; and L is 1,2-ethenediyl, 1,4-butadienediyl, 1,4-benzenediyl, 2,6-naphthalendiyl, 9,10-anthracenediyl, 2,7-fluorenediyl, 2,5-furandiyl, 2,5-thiophenediyl, 2,5-pyrroldiyl, 2,1,3-benzothiadiazole-4,7-diyl, 2,7-carbazolediyl, 2,6-pyridinediyl, 1,4-bis(2',2''-thiophenyl)benzene-5',5''-diyl, or 4,7-*bis*-(2',2''thiophenyl)-2,1,3-benzothiadiazole-5',5''-diyl that is unsubstituted or substituted. Exemplary L groups are given in Figure 1.

In an embodiment of the invention L is a substituted 2,5-thiophenediyl having the structure:



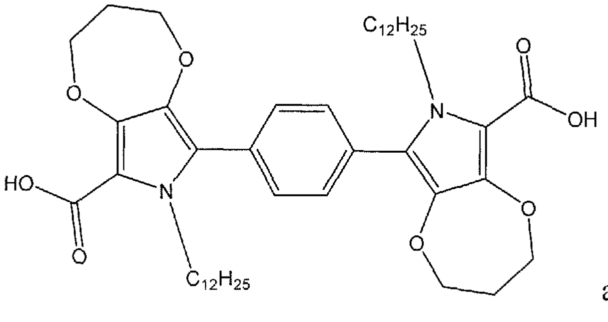
(V) or



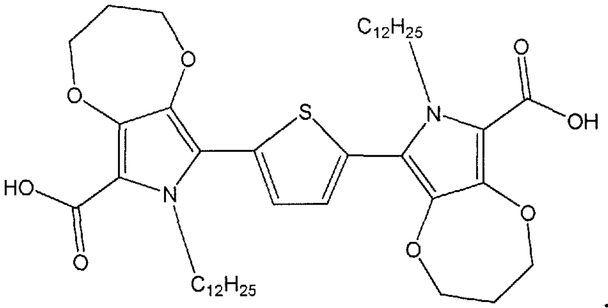
(VI)

where p is 2 through 6, m is 1 through p-1, n is 0 through p-2 and R^{18}, R^{19}, R^{20}, and R^{21} are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; and R^{22} and R^{23} are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl.

Examplary trimeric bis-dioxypyrroles, according to embodiments of the invention, include:



and



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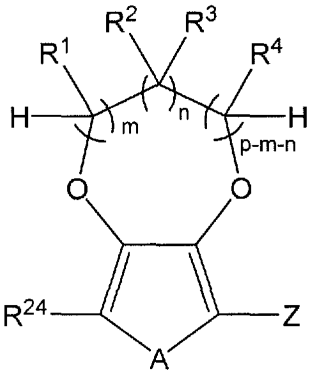
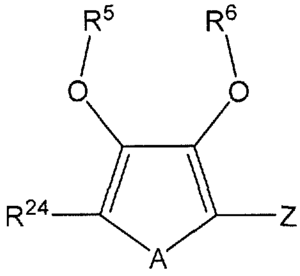
In embodiments of the invention, polymers are prepared from the homopolymerization of any trimer or the copolymerization of one or more trimers of the structures III or IV, for example, two or more different trimers of structure III, a trimer of structure III and a trimer of structure IV, or two trimers of the structure IV with a trimer of the structure III, or any other combination. In other embodiments of the invention, polymers are prepared from the copolymerization of one or more trimers of the structures III or IV with one or more dioxypyrrole monomers or oligomers of structures I and II. In an embodiment of the invention, the conjugated polymers have repeating units common with those of structures I, II, III, and/or IV from which they are prepared, and can have end-groups selected from H, C(O)OR^7, Cl, Br, and/or I.

In embodiments of the invention, an end-capping monomer of the structure is:



(VII) or



(VIII)

where R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; Z is H, chlorine, bromine, iodine, or $C(O)OR^7$ where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium, where 1 to 4 of the substituents on the ammonium is H, C_1 to C_8 alkyl, aryl, or alkyl aryl groups; A is O or NR, wherein R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X wherein X is $C(O)R^8$, CH_2YR^9, or CR^{10}=$CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, wherein Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$,and where R^9, R^{10}, R^{11}, R^{12}, R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl; and where R^{24} is C_1 through C_8 alkyl, aryl, alkylaryl, aryl, functional alkyl, functional aryl, or functional alkylaryl group, where the functional alkyl, functional aryl, or functional alkylaryl group have one or more functionalities selected from amines, acrylates, hydroxys, esters, carboxylic acid, thiols, enes, dienes, ynes, and halides.

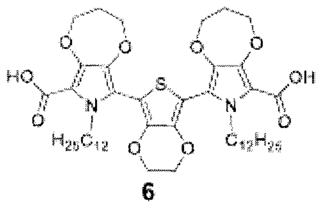
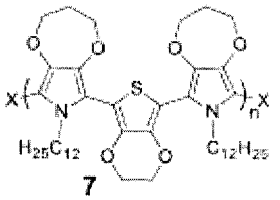
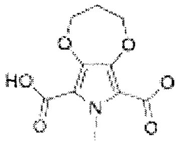
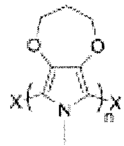
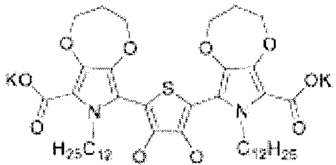
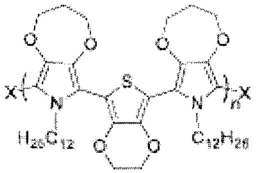
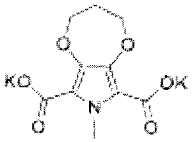
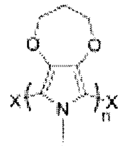
In an embodiment of the invention, the homopolymers or copolymers prepared from I, II, III, and/or IV, can be employed as macromers for their homopolymerization or their copolymerization with other monomers or oligomers from I, II, III, or IV to form higher molecular weight homopolymers, di- to multiblock copolymers, semi-random copolymers or semi-regular copolymers. In an embodiment of the invention, polymers prepared with one or more of I, II, III, and IV with VII and/or VIII have functionality for condensation, addition, or complexation with other monomers, oligomers, polymers, resins, surfaces, salts, or particles to form coupled polymers, block copolymers, multiblock copolymers, networks, aggregates, functionalized resins, functionalized surfaces, or functionalized particles.

Reynolds *et al.*, U.S. Patent No. 7,649,076 teaches the catalyst free polymerization of 2,5-dihalo-3,4-alkylenedioxypyrroles and 2,5-dihalo-3,4-alkylenedioxyfurans. This method involves isolation of the dihalo monomers, in the manner taught by Zong *et al. J. Org. Chem.* **2001**, *66*, 6873-82, as illustrated in Figure 2. After isolation, the polymerization is carried out, as indicated in Figure 2. The polymerization method has been successfully applied for the preparation of homopolymers and copolymers, either block or random copolymers.

However, a polycondensation method for production of regioregular copolymers from discrete α,ω-dihalo oligomers does not readily occur. Using the method of Zong *et al.*, it is not possible to prepare α,ω-dihalo oligomers, such as the trimers of structure III where Z is iodine, because a significant amount of decarboxylation of the diacid occurs during the first step of base catalyzed ester hydrolysis to the diacid, which leads to a mixture of products even when the hydrolysis is carried out at relatively low temperatures. Preparation of *N*-alkyl substituted 3,4-alkylenedioxypyrrole monomers that can be used to prepare polymers, according to embodiments of the present invention, are taught in Reynolds *et al.*, U.S. Patent No. 7,799,932, and incorporated herein by reference.

It was discovered that *N*-halosuccinimides promote electrophilic halogenation of a model 3,4-propylenedioxypyrrole (ProDOP) **9** and halodecarboxylation of a model 3,4-propylenedioxypyrrole carboxylic acid **8**, as shown in Figure 3, and that *N*-halosuccinimides promote halodecarboxylation of a model 3,4-propylenedioxypyrrole carboxylic acid potassium salt **10**, as shown in Figure 4. While attempting to extend the *N*-halosuccinimides promoted electrophilic halodecarboxylation to ProDOP-dicarboxylates, either acids or potassium salts, polymerization resulted, according to an embodiment of the invention, and polymerization can be carried out effectively using *N*-iodosuccinimide (>2 equivalents) or iodine (>2 equivalents) to high molecular weight polymer, as shown in Figure 5. Results for polymerization of monomeric and trimeric dicarboxylic acids and di(potassium carboxylates) are given in Table 1, below. The polymerization occurs at relatively low temperatures, for example, 40 to 60 °C or below, in dichloromethane (DCM) or chloroform. Potassium carboxylates, such as **14** and **17,** have low solubility in DCM and the reaction can be carried out in an emulsion formed with water and DCM. Other solvents, for example THF, can be used.

Table 1 Polymerization of various ProDOP-dicarboxylates *via* halodecarbonylation-dehalogenation polycondensation using various halogen (X) sources

entry	monomer	X-Source	polymer	*Mn* / *Mw* (kDa)	yield[a] (%)
1	 **6**	NIS NBS NCS	 **7**	**7a** 7.7/13.6 **7b** 66.3/8.9 **7c** 5.0/6.3	71[b] 83[b] 39[b]
2	 **15**	NIS NBS NCS	 **16**	**16a** 6.9/17.4 **16b** 0.9/1.1 **16c** 1.1/1.5	60 76[c] 79[c]
3	 **14**	NIS I_2 Br_2	 **7**	**7a** 6.2/10.0 **7a** 22.9/58.1 **7b** 1.3/1.9	67 66 20[c]
4	 **17**	I_2 Br_2	 **16**	**16a** 15.9/35.7 **16b** 0.9/1.9	55 48

[a]The yields were calculated based on the potassium salts except for entry 2, by the method of Walczak *et al., Macromolecules* **2008**, *41*, 691-700. [b]The crude mixture was employed after acidic work-up of the respective potassium salt. [c]The polymer was not precipitated but was washed with water and methanol, and dried under vacuum.

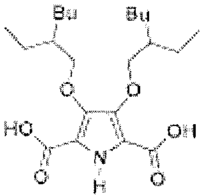
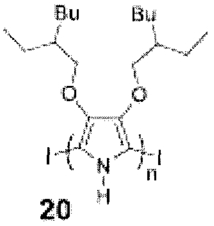
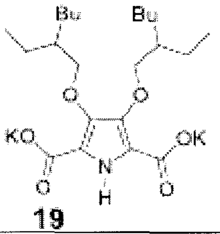
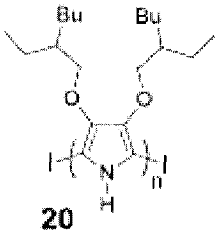
Polymerizations using *N*-iodosuccinimide (NIS) require longer reaction times than did those using iodine, at otherwise equivalent conditions. *N*-Chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS), and bromine produce lower molecular weight polymers. The polymerization typically starts spontaneously, but, if needed or desired, can be promoted by irradiation with UV-light using a standard UV-lamp, typically requiring only a few minutes of irradiation, for example, 1 to 3 minutes, to promote polymerization. A catalytic amount of $FeCl_3$ can be added to the monomer mixture to promote the polymerization. The polymer that is produced is halogen doped, which can be easily dedoped by the addition of hydrazine.

Although no specific relationship has been determined between the number of equivalents of halogen from the halogen source and the molecular weight of the polymer, when less than two equivalents of halogen is employed, the resulting molecular weight of the polymer is less than when more than two equivalents are employed. End-groups of the polymer are indicated as X in Table 1, and are halogens or a starting carboxylate groups.

Conditions of the polymerization affect the degree of polymerization obtained and allow the use of the oligomers or polymers that are produced in one polymerization to be used as macromers for the formation of larger homopolymers or block copolymers. As shown in Figure 6, polymer **7a** with a molecular weight of about 7 kDa, can be used as a macromer to produce a polymer of 11 kDa. The macromer **7a**, as shown in Figure 6, was prepared in DCM, reduced with hydrazine, precipitated in MeOH, and stored under argon for several months before carrying out its polymerization in dibromomethane, at a temperature in excess of the boiling point of DCM.

Employing *N*-protonated 2,5-disubstituted-3,4-alkylenedioxypyrroles results in polymers, although generally of lower molecular weight than those of *N*-alkylated 2,5-disubstituted-3,4-alkylenedioxypyrrole, as indicated in Table 2, below. However, compared to the $FeCl_3$ oxidative polymerization of 3,4-dioxypyrroles, as taught in Kim *et al.*, *Chem. Lett.* **2004**, *33*, 46-7, a polymerization by any embodiment of the present invention, can provide higher molecular weights and permits polymerizations starting from 3,4-dioxypyrroles carboxylates, which are the normal precursors to unsubstituted 3,4-dioxypyrroles used in $FeCl_3$ oxidative polymerizations. Furthermore, the halodecarbonylation-dehalogenation polycondensation method, according to embodiments of the invention, displays higher tolerance to functionality and lower sensitivity toward water than is observed with other methods for the polymerization of 3,4-dioxypyrroles.

Table 2 Polymerization of *N-H*-3,4-alkydioxypyrroles *via* halodecarbonylation-dehalogenation polycondensation using NIS and iodine

monomer	I-Source	polymer	*Mn* / *Mw* (kDa)	yield[a] (%)
 **18**	NIS	 **20**	3.7 / 5.2	31[b]
 **19**	I_2	 **20**	2.1/2.8	36[b]

[a]Yields were calculated as in Table 1. [b]Polymer was isolated by removal of the solvent *in vacuo*, washing with water and methanol, and drying under vacuum.

Polymeric materials comprising 3,4-dioxypyrroles possess characteristic optical and electrochemical properties, as indicated in the spectroelectrochemistry data for polymer **7a** that is shown in Figure 7. This polymeric material: is almost colorless in solution and the solid state; can be employed as a film on an ITO-coated glass or other transparent electrode; and displays almost no absorption in the visible region of the light spectrum. As shown in Figure 7a, upon electrochemical oxidation, polymer **7a** remains highly transmissive in the visible region with absorption in the near infrared region. Minimum color changing polymer, such as **7a**, may be used for applications in organic electronics, such as in electrochromic devices and windows. The cyclic voltammetry on ITO, of Figure 7b, shows that polymer **7a** has a low oxidation potential (+0.18V vs. Ag/Ag+), for this electron rich polymeric system. Under conditions of the electrochemical experiment, polymer **7a** delaminated from the ITO slide upon electrochemical oxidation, consistent with a high solubility of the doped polymer in the solvent, acetonitrile, that was used.

Polymers prepared according to embodiments of the invention can comprise materials that are advantageous for electrochromic windows, mirrors or displays. Additionally, these polymers can comprise materials for field effect transistors, supercapacitors, batteries, or other electronic devices. The polymers, according to embodiments of the invention, can comprise materials used in electronic paper, camouflage, anti-stat conductors, or photovoltaic devices.

METHODS AND MATERIALS

All reagents and starting materials were purchased from commercial sources and used without further purification unless otherwise noted. All reactions were carried out under argon atmosphere unless otherwise noted. All ^{1}H-NMR and ^{13}C-NMR spectra were generated using a Mercury 300 or Inova 500 NMR Spectrometer. Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida. FTIR measurements were carried out using a Perkin-Elmer Spectrum One FTIR outfitted with a $LiTaO_3$ detector. Gel permeation chromatography (GPC) was performed using a Waters GPCV2000 liquid chromatography system with an internal differential refractive index detector (DRI) with two Waters Styragel HR-5E columns in series (10 μm PD, 7.8 mm i.d., 300 mm length) and a mobile phase of tetrahydrofuran (THF) with a flow rate of 1.0 mL/min, by injection of samples have a concentration of 0.05 - 0.08 % w/v. Retention times were calibrated against narrow molecular weight polystyrene standards.

Monomer syntheses.

Dioxypyrrole potassium salts and diacids were synthesized from their respective diesters, as previously reported in Arroyave *et al.*, *J. Org. Chem.* **2011**, *76*, 8621-28.

5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylic acid) (6a).

The potassium dicarboxylate **14** of **6** (0.133 g, 0.1449 mmol, 1 equiv.), 10 mL of water, and 20 mL of dichloromethane DCM were added to and shaken in a 100-mL separatory funnel. To the mixture was added 20 mL of 0.5M HCl and the mixture shaken. After separation of the layers, the DCM layer was removed. The remaining aqueous layer was combined and shaken with an additional 20 mL of DCM and 10 mL of 0.5M HCl and upon separation, the DCM layer was removed and combined with the first DCM layer. The combined DCM solution was washed three times with deionized water, and dried using sodium sulfate. The DCM was removed *in vacuo*, and the resulting solid was dried under vacuum for an additional two hours. The product was obtained as a mixture of diacid **6a**, monoacid **6b** and non-substituted dioxypyrrole oligomer **6c**. The product was used without further purification. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 9.77 (br, 1.23H), 6.33 (s, 0.17H), 6.31

(s, 0.05H), 4.26 (m, 11.52H), 4.05 (m, 4.43H), 3.71 (m, 0.84H), 2.26 (m, 4H), 1.62 (m, 4.25H), 1.45 – 1.19 (br, m, ~ 38.15H), 0.86 (t, 6H, J = 6.14). ^{13}C-NMR (75 MHz, $DCCl_3$): δ_C 159.7, 141.9, 139.9, 135.4, 117.3, 107.7, 105.5, 73.8, 72.2, 64.8, 46.4, 34.3, 32.1, 31.7, 29.9, 29.8, 29.6, 29.5, 26.9, 22.9, 14.3. Figures 8 and 9 are traces of the ^{1}H-NMR spectrum and the ^{13}C-NMR spectrum, respectively.

Polymerization method using *N*-halosuccinimides

Poly(2,5-(5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole))) 7a

The crude diacid **6** (0.122 g, 0.1449 mmol, 1 equiv.) and 2 mL DCM (or chloroform) were added to a 25-mL round bottom flask equipped with a stir bar and a condenser and under an argon atmosphere. The flask was cooled to -20 °C, and *N*-iodosuccinimide (0.069 g, 0.3043 mmol, 2.1 equiv., freshly recrystallized from dioxane) was added in a single portion. The reaction mixture was stirred for 10 minutes, slowly warmed to 60 °C, and stirred for 4 days. The reaction mixture was cooled to room temperature and cold hydrazine monohydrate was added with caution. The resulting mixture was poured in methanol (120 mL) and stirred for 30 minutes when the polymer precipitated. The resulting solid was collected by vacuum filtration, washed with methanol, dissolved in 2 mL of THF, and precipitated by addition to MeOH. The precipitate was filtered using a 20-µm nylon membrane filter, washed with MeOH, and dried under vacuum. A pale yellow solid, 80 mg, was recovered, 71% yield, M_n = 7675, and M_w = 13599. ^{1}H-NMR (500 MHz, $DCCl_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br, 40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 138.5 (br), 137.9 (br), 137.2 (br), 112.6, 109.2 (br), 107.0, 72.3 (br), 64.7 (br), 45.7 (br), 35.3 (br), 32.2, 31.4, 31.0, 29.9 (br), 29.7, 29.6 (br), 28.9, 27.2 (br), 26.9, 26.8, 22.9, 14.3. Elemental Analysis calculated for $C_{44}H_{66}N_2O_6S$: C (70.36%), H (8.86%), N (3.73%). Found: C (70.32%), H (8.96%), N (3.52%). Figures 10, 11, and 12 are traces of the GPC chromatograph, ^{1}H-NMR spectrum, and ^{13}C-NMR spectrum, respectively.

Poly(2,5-(5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole))) 7b

The reaction was carried out using the same procedure for polymer **7a**, above, where an equivalent molar quantity of *N*-bromosuccinimide was substituted for *N*-iodosuccinimide. A pale yellow solid was recovered in 83% yield. M_n = 6300, M_w = 8898. ^{1}H-NMR (500 MHz, $DCCl_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br, 40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, DCCl$_3$): 138.5 (br), 137.9 (br), 115.9 (br), 109.0 (br), 72.3, 64.7, 45.7, 35.3, 32.2, 31.0, 30.5, 29.9, 29.6, 29.2, 29.1, 28.9, 27.2, 27.1, 27.0, 22.9, 14.3.

Poly(2,5-(5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole))) 7c

The reaction was carried out using the same procedure for polymer **7a**, above, where an equivalent molar quantity of *N*-bromosuccinimide was substituted for *N*-chlorosuccinimide. A pale yellow solid was recovered in 39% yield. $M_n = 4978$, $M_w = 6291$. ^{1}H-NMR (500 MHz, DCCl$_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br, 40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, DCCl$_3$): 138.3 (br), 137.9 (br), 137.2 (br), 119.8 (br), 109.1 (br), 109.0 (br), 72.3, 64.7, 45.7, 35.3, 32.2, 31.0, 30.7, 29.9, 29.7, 29.6, 29.1, 29.0, 27.3, 22.9. 14.3.

Poly(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole)) 16a using *N*-iodosuccinimide

Reaction and isolation were carried out using the same procedures for polymer **7a**, above, with a 60% yield. $M_n = 13980$, $M_w = 16781$. ^{1}H-NMR (500 MHz, DCCl$_3$): δ_H 4.38 – 3.20 (m, br, 6H), 2.15 (s, br, 2H), 1.74 – 0.95 (m, br, 20H), 0.86 (s, br, 3H). ^{13}C-NMR (125 MHz, DCCl$_3$): 139.0, 109.1, 72.2, 46.1, 35.3, 32.2, 30.8, 30.1, 30.0, 29.9, 29.7, 29.6, 27.1, 22.9, 14.3. Elemental Analysis calculated for $C_{19}H_{31}NO_2$: C (74.71%) H (10.63%) N (4.21%). Found: C (74.58%), H (10.73%), N (4.34%).

Poly(*N*-*H*-3,4-(di-2-ethylhexoxypyrrole)) 20 using *N*-iodosuccinimide

Reaction was carried out using the same procedure for polymer **7a**, above, and isolation involved: reduction with cold hydrazine monohydrate and addition of the reaction mixture dropwise to 75 mL of MeOH in an Erlenmeyer flask. The mixture was stirred for 20 minutes, and decanted. A sticky oil that remained in the Erlenmeyer flask was washed with 40 mL of MeOH, dissolved using THF, the solution transferred to a vial, the solvent removed *in vacuo*, and the product stored under argon. The product was received as a brown-black sticky solid, 31% yield. $M_n = 3646$, $M_w = 5222$. ^{1}H-NMR (500 MHz, DCCl$_3$): δ_H 9.68 – 8.60 (s, br, 1H), 4.37 – 3.57 (m, 4H), 2.04 – 1.09 (m, 18), 0.84 (m, 12). ^{13}C-NMR (125 MHz, DCCl$_3$): δ_C 131.1, 129.0, 40.3, 30.4, 29.2, 23.6 (br), 23.3, 14.3, 11.0. FTIR (NaCl, disc) $^{\mathrm{v}}$(cm^{-1}): 3436.8 (w), 2958.0 (s), 2929.6 (s), 2873.6 (s), 2856.5 (s), 1717.5 (w), 1605.4 (m, br), 1464.4 (s, br), 1379.2 (s), 1343.8 (m), 1194.7 (m), 1112.1 (s), 1051.0 (s), 772.1 (w), 728.0 (w).

General polymerization method using iodine

Poly(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole)) 16a

ProDOP potassium salt **17** (0.200 g, 0.4240 mmol, 1.0 equiv.), iodine (0.226 g, 0.8905 mmol, 2.0 equiv), and 2 mL of DCM were added to a 25-mL round bottom flask equipped with a stir bar and a condenser under an argon atmosphere. The reaction mixture was stirred at room temperature for 10 minutes and 2 mL of deionized water was added. The reaction was warmed to 60 °C, and stirred for 48 hours. The reaction mixture was allowed to cool to room temperature and reduced by careful addition of 2 mL of cold hydrazine monohydrate. The crude mixture was added to 75 mL of methanol and stirred for 15 minutes and the polymer precipitated. The resulting solid was collected by filtration using a 20 μm nylon membrane, dissolved in 2 mL of THF, and precipitated in 75 mL of MeOH. The solid was collected by filtration using a 20 μm nylon membrane and subjected to Soxhlet extraction using MeOH for 16 hours. The resulting solid was dissolved with dichloromethane and reduced dropwise with hydrazine monohydrate if the solution became dark. The solution was concentrated to approximately 2 mL and precipitated into 50 mL of methanol. The resulting solid was collected by filtration using a 20 μm nylon membrane and dried under vacuum. The product was isolated as a pale yellow solid, 0.072 g, 55% yield. $M_n = 15909$, and $M_w = 35718$. ^{1}H-NMR (500 MHz, $DCCl_3$): δ_H 4.30 – 3.20 (m, br, 6H), 2.14 (s, br, 2H), 1.70 – 0.90 (m,br, 20H), 0.85 (s, br, 3H). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 138.3 (br), 109.1 (br), 108.6 (br), 72.2, 72.1, 45.7, 35.4, 32.2, 31.3, 30.8, 30.0, 29.6, 27.4, 27.1, 22.9, 14.3. Elemental Analysis calculated for $C_{19}H_{31}NO_2$: C (74.71%) H (10.63%) N (4.21%). Found: C (74.71%), H (10.23%), N (4.59%). Figures 13, 14, and 15 are traces of the GPC chromatograph, ^{1}H-NMR spectrum, and ^{13}C-NMR spectrum, respectively.

Poly(2,5-(5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole))) 7a

Reaction was carried out using the same procedure for polymer **16a**, above, resulting in a 66% yield. $M_n = 22875$, $M_w = 58099$. ^{1}H-NMR (500 MHz, $DCCl_3$): δ_H 4.5 – 3.48 (m, br, 16H), 2.19 (s, br, 2H), 2.09 (s, br, 2H), 1.68 – 1.00 (m, br, 40), 0.86 (t, 6H, J = 6.9 Hz). ^{13}C-NMR (125 MHz, $DCCl_3$): δC 131.1, 129.0, 40.3, 30.4, 29.2, 23.6 (br), 23.3, 14.3, 11.0.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

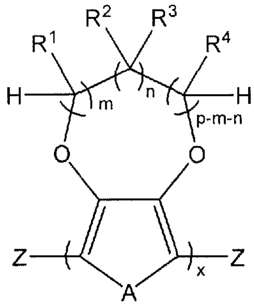
It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

CLAIMS

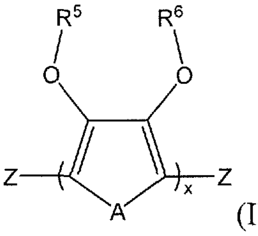
We claim:

1. A method for the preparation of a polymer comprising:

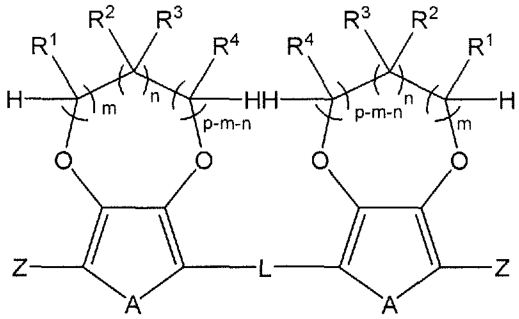
providing a plurality of monomers and/or oligomers of the structure:



(I);

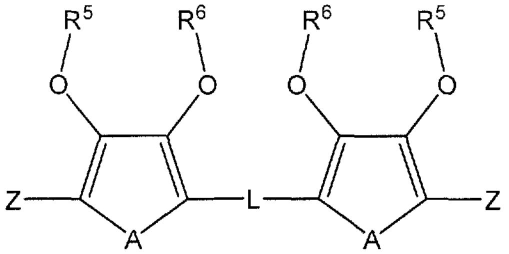


(II);



(III);

and/or



(IV),

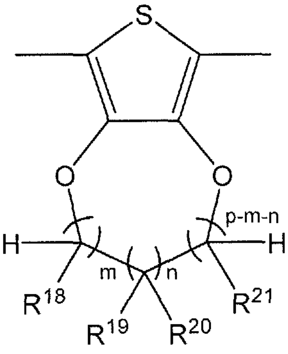
where: x is 1 to 10; R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; when x is 1, Z is H or $C(O)OR^7$, or when x is absent or > 1, Z is H, chlorine, bromine, iodine, or $C(O)OR^7$, where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium where 1 to 4 of the bonds to N is to H, C_1 to C_8 alkyl, aryl, or alkyl aryl groups; A is O or NR, where R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X wherein X is $C(O)R^8$, CH_2YR^9, or $CR^{10}{=}CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, wherein Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$, and where R^9, R^{10}, R^{11}, R^{12} ,R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl;

and L comprises an unsubstituted or substituted 1,2-ethenediyl, 1,4-butadienediyl, 1,4-benzenediyl, 2,6-naphthalendiyl, 9,10-anthracenediyl, 2,7-fluorenediyl, 2,5-furandiyl, 2,5-thiophenediyl, 2,5-pyrroldiyl, 2,1,3-benzothiadiazole-4,7-diyl, 2,7-carbazolediyl, 2,6-pyridinediyl, 1,4-bis(2',2''-thiophenyl)benzene-5',5''-diyl, or 4,7-*bis*-(2',2''thiophenyl)-2,1,3-benzothiadiazole-5',5''-diyl;

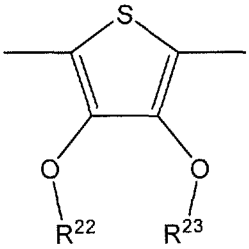
providing at least two equivalents of a halogen, *N*-haloimide, or *N*-haloamine for every mole of the monomers and/or oligomers; and

polymerizing or copolymerizing the monomers and/or oligomers to form a conjugated polymer.

2. The method of claim 1, wherein L is the substituted 2,5-thiophenediyl of the structure:



(V) or



(VI),

where p is 2 through 6, m is 1 through p-1, n is 0 through p-2 and R^{18}, R^{19}, R^{20}, and R^{21} are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; and R^{22} and R^{23} are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl.

3. The method of claim 1, wherein the conjugated polymer is a homopolymer from the monomer of structure I or II, wherein x is 1, A is NR, and Z is $C(O)OR^7$.

4. The method of claim 1, wherein the conjugated polymer is a homopolymer or a copolymer from the monomer of structure III or IV, wherein A is NR and Z is $C(O)OR^7$.

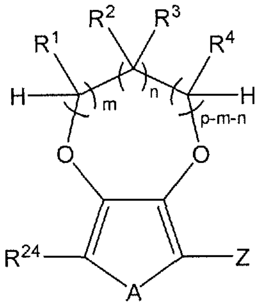
5. The method of claim 1, wherein the conjugated polymer is a copolymer from a plurality of the monomers of structures I and/or II, wherein x is 1, A is NR, and Z is $C(O)OR^7$.

6. The method of claim 1, wherein the conjugated polymer is a copolymer from a plurality of the monomers of structures III and IV, wherein A is NR, and Z is $C(O)OR^7$.

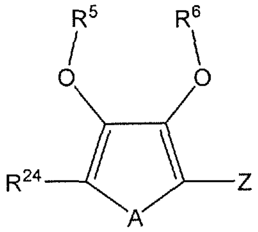
7. The method of claim 1, wherein the conjugated polymer is a copolymer from at least one of the monomers of structures I and II and at least one of the monomers of structures III or IV, wherein x is 1, A is NR, and Z is $C(O)OR^7$.

8. The method of claim 1, wherein the conjugated polymer comprises halogen end-groups of the halogen, *N*-haloimide or *N*-haloamine provided.

9. The method of claim 1, further comprising an end-capping monomer of the structure:



(VII) or



(VIII)

where R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; Z is H, chlorine, bromine, iodine, or $C(O)OR^7$ where R^7 is hydrogen, lithium, sodium, potassium, cesium, or ammonium where 1 to 4 of the bonds to N is H, C_1 to C_8 alkyl, aryl, or alkyl aryl groups; A is O or NR, wherein R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X wherein X is $C(O)R^8$, CH_2YR^9, or $CR^{10}=CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, wherein Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$,and where R^9, R^{10}, R^{11}, R^{12} ,R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl; and R^{24} is alkyl, aryl, alkylaryl, aryl, functional alkyl, functional aryl, or functional alkylaryl group, wherein the functional alkyl, the functional aryl, or the functional alkylaryl group comprises one or more functional groups selected from amines, acrylates, hydroxys, esters, carboxylic acid, thiols, enes, dienes, ynes, and halides.

10. The method of claim 1, further comprising providing an acid.

11. The method of claim 1, further comprising irradiating with ultraviolet light.

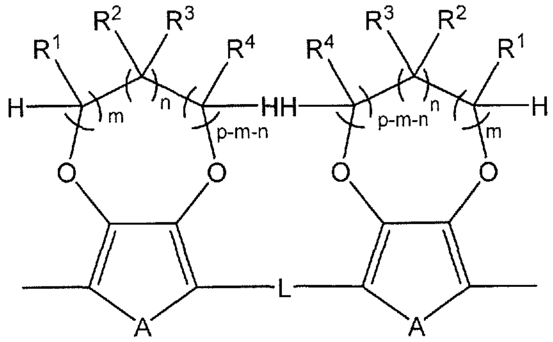
12. The method of claim 1, further comprising providing a solvent.

13. The method of claim 1, wherein polymerizing or copolymerizing is carried out under an inert atmosphere or under air.

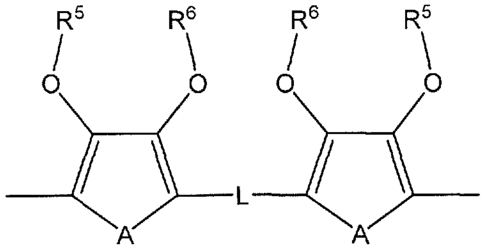
14. The method of claim 1, wherein polymerizing or copolymerizing is carried out at 0 to 100 °C.

15. A conjugated polymer, comprising:

a multiplicity of repeating units of the structure:



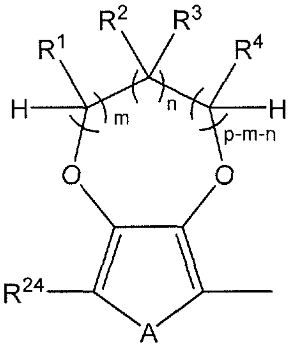
and/or



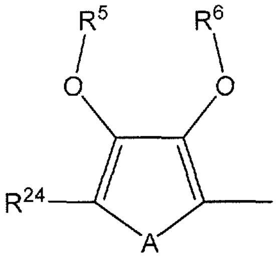
where: R^1, R^2, R^3, and R^4 are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; R^5 and R^6 are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; p is 2 through 6, m is 1 through p-1, n is 0 through p-2; A is O or NR, wherein R is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, alkylaryl, or CH_2X wherein X is $C(O)R^8$,

CH_2YR^9, or CR^{10}=$CR^{11}R^{12}$, where R^8 is hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, OR^{13}, or $NR^{14}R^{15}$, where R^{13}, R^{14}, and R^{15}, are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl or alkylaryl, wherein Y is O, OC(O), NR^{16}, or $NR^{17}C(O)$, and where R^9, R^{10}, R^{11}, R^{12} ,R^{16}, and R^{17} are independently hydrogen, methyl, ethyl, C_3 through C_8 straight or branched chain alkyl, aryl, or alkylaryl; and L comprises an unsubstituted or substituted 1,2-ethenediyl, 1,4-butadienediyl, 1,4-benzenediyl, 2,6-naphthalendiyl, 9,10-anthracenediyl, 2,7-fluorenediyl, 2,5-furandiyl, 2,5-thiophenediyl, 2,5-pyrroldiyl, 2,1,3-benzothiadiazole-4,7-diyl, 2,7-carbazolediyl, 2,6-pyridinediyl, 1,4-bis(2',2''-thiophenyl)benzene-5',5''-diyl, or 4,7-*bis*-(2',2''thiophenyl)-2,1,3-benzothiadiazole-5',5''-diyl; and

optionally one or more end-groups comprising chlorine, bromine, iodine,



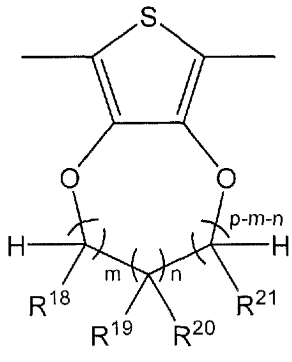
and/or



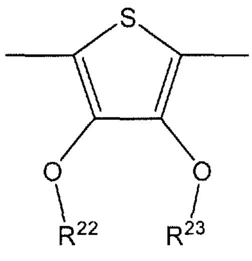
,

where R^{24} is alkyl, aryl, alkylaryl, aryl, functional alkyl, functional aryl, or functional alkylaryl group, wherein the functional alkyl, the functional aryl, or the functional alkylaryl group comprises one or more functional groups selected from amines, acrylates, hydroxys, esters, carboxylic acid, thiols, enes, dienes, ynes, and halides.

16. The conjugated polymer of claim 15, wherein L is



(V) and/or



(VI),

where p is 2 through 6, m is 1 through p-1, n is 0 through p-2 and R^{18}, R^{19}, R^{20}, and R^{21} are independently hydrogen, methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl; and R^{22} and R^{23} are independently methyl, ethyl, C_3 through C_{20} straight or branched chain alkyl, aryl, or alkylaryl.

AMENDED CLAIMS

received by the International Bureau on 12 July 2013 (12.07.2013)

Claim 1 A portable media delivery system comprising:

a plastic chamber having a wall thickness of between 0.080 and 0.400 inches thick containing media within an interior of said plastic chamber;

said plastic chamber is molded and after said plastic chamber is molded, said plastic chamber is further thermal treated at a temperature of between 50 to 300 degrees Centigrade;

a port having a first end located on the exterior of said plastic chamber where said first end connects to a replaceable pressure filled cylinder and a second end that extends to an interior of said plastic chamber, and

whereby when said pressure filled cylinder is ruptured, contents of said pressure filed cylinder vents into said port and into said interior of said plastic chamber to expel said media out of an operable exit port of said plastic chamber.

Claim 2 The portable media delivery system according to Claim 1 in which said plastic chamber is molded plastic.

Claim 3 The portable media delivery system according to Claim 1 in which said operable exit port can be closed and opened.

Claim 4 The portable media delivery system according to Claim 1 wherein when said replaceable pressure filled cylinder is vented within a closed said plastic chamber said closed plastic chamber is pressurized to between 15 and 150 psi.

Claim 5 The portable media delivery system according to Claim 1 wherein said replaceable pressure filled cylinder has an internal volume of between 30 to 100 ml.

Claim 6 The portable media delivery system according to Claim 5 wherein said replaceable pressure filled cylinder is filled with between 10 and 100 grams of air or gas under pressure of at least 600psi at 70 degrees Fahrenheit.

Claim 7 The portable media delivery system according to Claim 1 wherein said plastic chamber has an internal volume of between 50 and 500 cubic inches.

Claim 8 The portable media delivery system according to Claim 7 wherein said internal volume includes between 5 to 100 cubic inches for delivery of said pressure filled cylinder to expel said media.

Claim 9 The portable media delivery system according to Claim 7 wherein said internal volume includes between 50 to 500 cubic inches of media.

Claim 10

Claim 11 The portable media delivery system according to Claim 1 wherein said plastic chamber is further thermal treated for between 15 minutes and 2 hours.

Claim 12 The portable media delivery system according to Claim 1 wherein said replaceable pressure filled cylinder is at least partially located within a handle of said portable fire extinguisher.

Claim 13 The portable media delivery system according to Claim 1 further having a bottom housing and a top housing that are connected with a quick disconnect.

Claim 14 The portable media delivery system according to Claim 13 wherein pressure filled cylinder is connected to said top housing with at least one bayonet, interlocking tabs, ears ball detents, and a hasp.

Claim 15 The portable fire extinguisher according to Claim 1that further includes a replaceable rupture pin that ruptures said Claim 1 replaceable pressure filled cylinder

Claim 16 The portable fire extinguisher according to Claim 15 wherein said replaceable rupture pin has at least one vent.

Claim 17 The portable fire extinguisher according to Claim 15 wherein said replaceable rupture pin is connected to said top housing with at least one bayonet, interlocking tabs, ears, ball detents, and a hasp.

Claim 18 The portable media delivery system according to Claim 15 wherein said replaceable rupture pin and said replaceable pressure filled cylinder are replaceable as a single unit.

Claim 19 The portable media delivery system according to Claim 1 wherein said plastic chamber is at least semi-transparent.

Claim 20 The portable media delivery system according to Claim 1 wherein said replaceable pressure filled cylinder is filed with a gas comprising at least one of oxygen, CO_2, Argon, Helium, and Nitrogen.

Statement under Article 19(1)

This listing of claims will replace all prior versions, and listings, of claims in the application: Where there were originally 20 claims and after amendment of claims there are 19. Claim 1 is changed. Claims 2 – 9 and 11 - 20 are unchanged. Claim 10 is canceled.

BASIS FOR THE AMENDMENTS

(i) Basis for the amendments regarding: Claim 1. The applicant has amended claims 10 in to claim 1 in lines 4 - 6, whereby cancelling claim 10. The applicant respectfully disagrees with the examiner that it is obvious to combine the plastic wall thickness of Tsuchida with the fire extinguisher of Rousseau. IN paragraph 10 of Tsuchida , Tsuchida states "...it is not easy to increase the thickness of the cylinder so as to satisfy the value of standard...". This statement clearly indicates that it is not "ordinary skill" to make the changes in wall thickness proposed by the examiner. The amendment of claim 10 was rejected by the examiner using the reference Reyes. In Reyes the processing temperature of the resin is between 200 and 210 degrees (Paragraph 49). This is not a thermal treating process that takes place after the plastic chamber is formed.

(ii) Basis for the amendments regarding: Claims 2 – 9 and 11 – 20 are unchanged and the applicant Supra the argument for allowability of claims 2 – 9 and 11 – 20 based upon dependence on claim 1. Claim 10 has been canceled on the basis that it has been combined into claim 1.

The examiner argues that the limitations of claims 2 – 9 and 11 – 20 involve only routine skill in the art to discover the optimum or workable ranges. The applicant respectfully disagrees with the examiner. There are multiple variable factors that are involved in establishing the specified ranges. Establishing one range affects several other working ranges. The determination of the ranges involves calculations, and real world testing. Combining these factors with the thermal treatment amendment in claim 1 further exacerbates identification of variables.

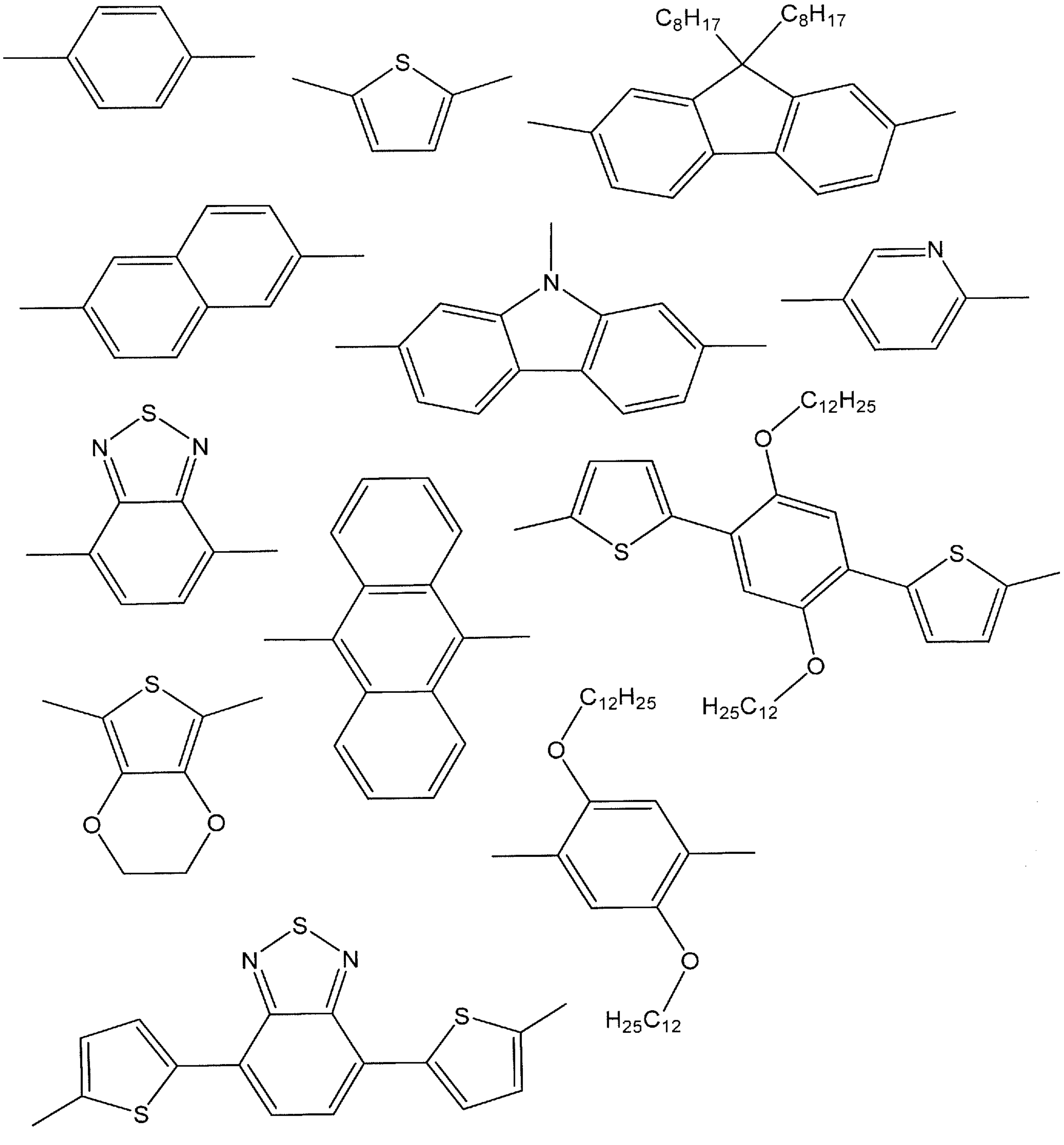

C8H17
C8H17
S
N
N
S
N
N
C12H25
O
S
S
O
H25C12
S
O
O
C12H25
O
O
H25C12
S
N
N
S
S

Figure 1

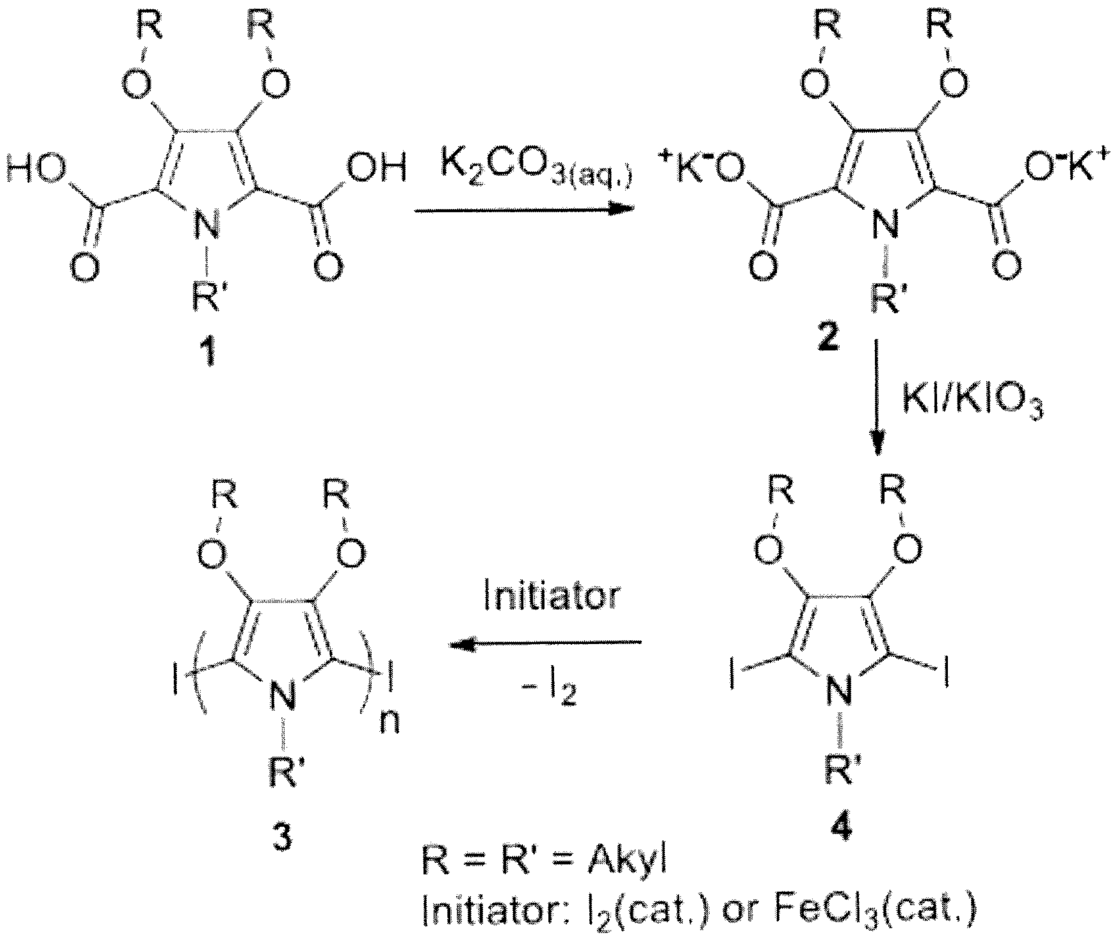


Figure 2
(prior art)

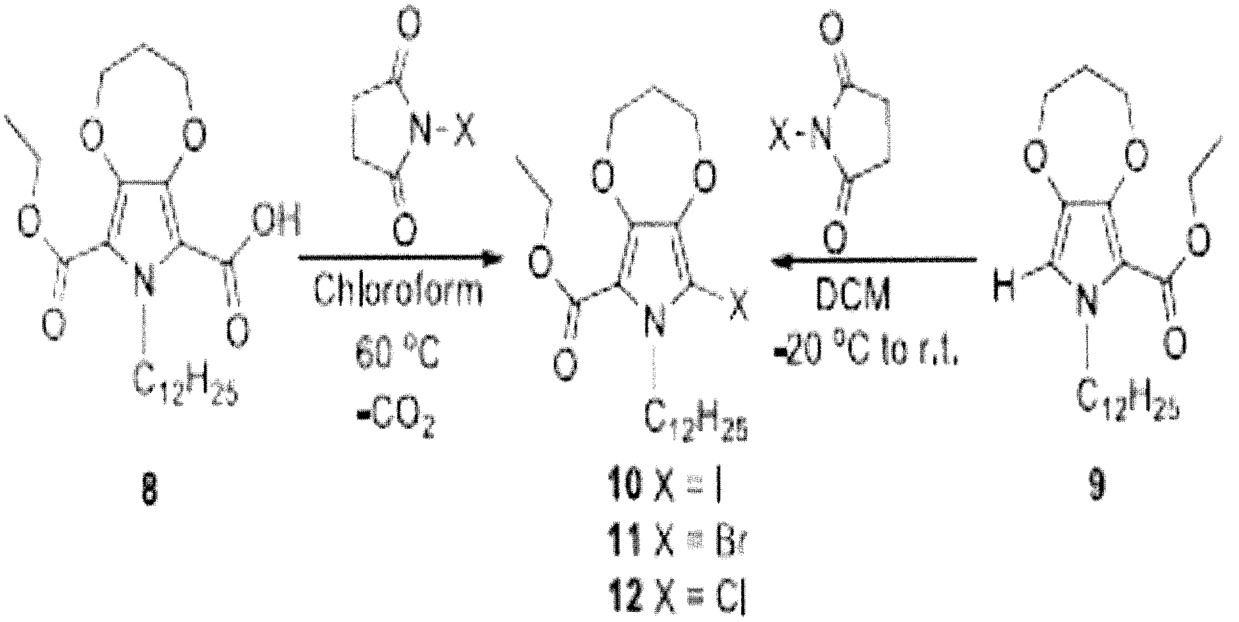


Figure 3

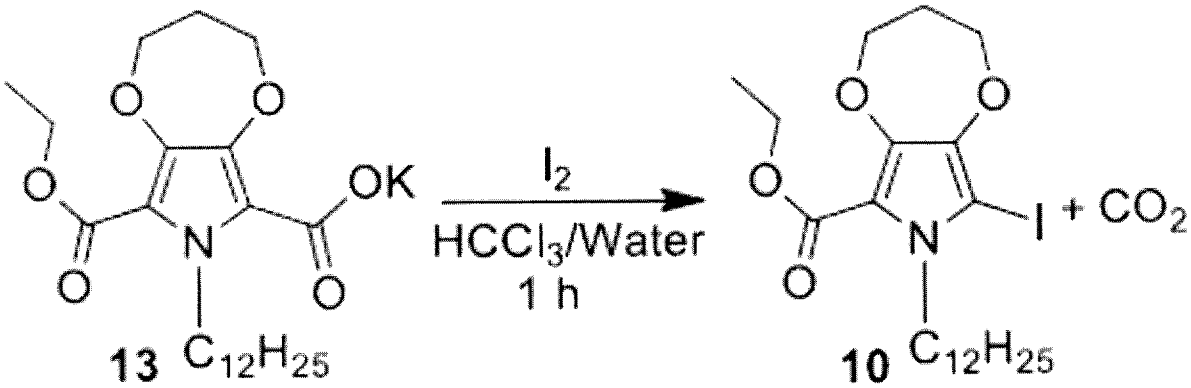
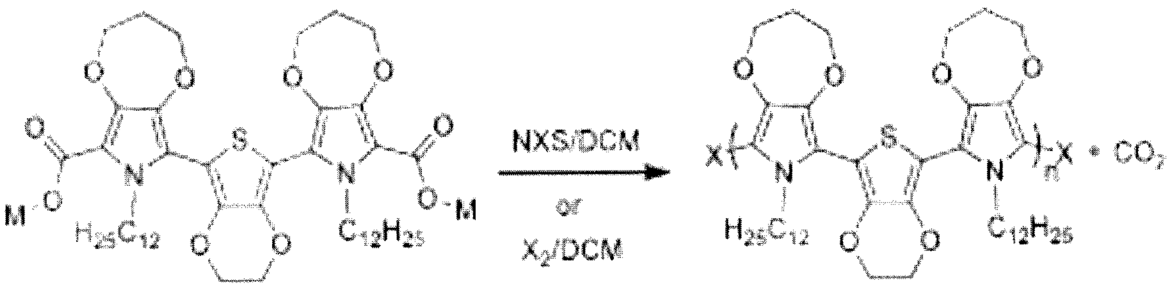


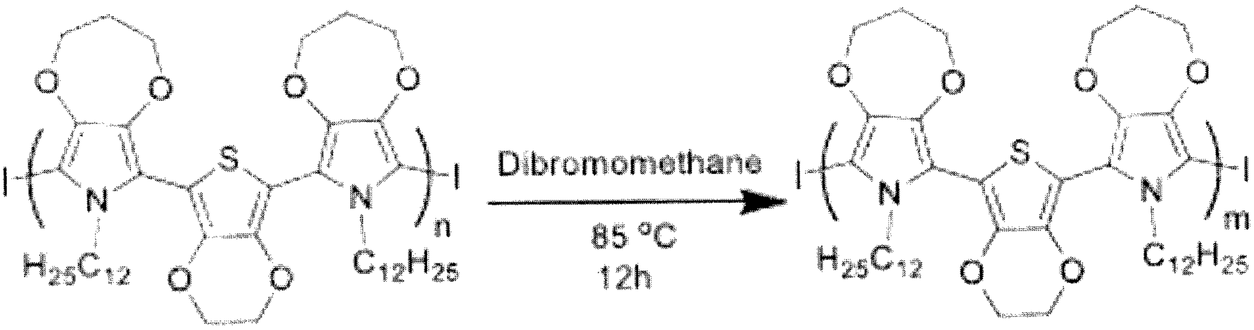
Figure 4



6 M = H
14 M = K

7a X = I
7b X = Br
7c X = Cl

Figure 5



7a Mn = 7.0K
Mw = 10..5K

Mn = 11.3K
Mw = 23.5K

Figure 6

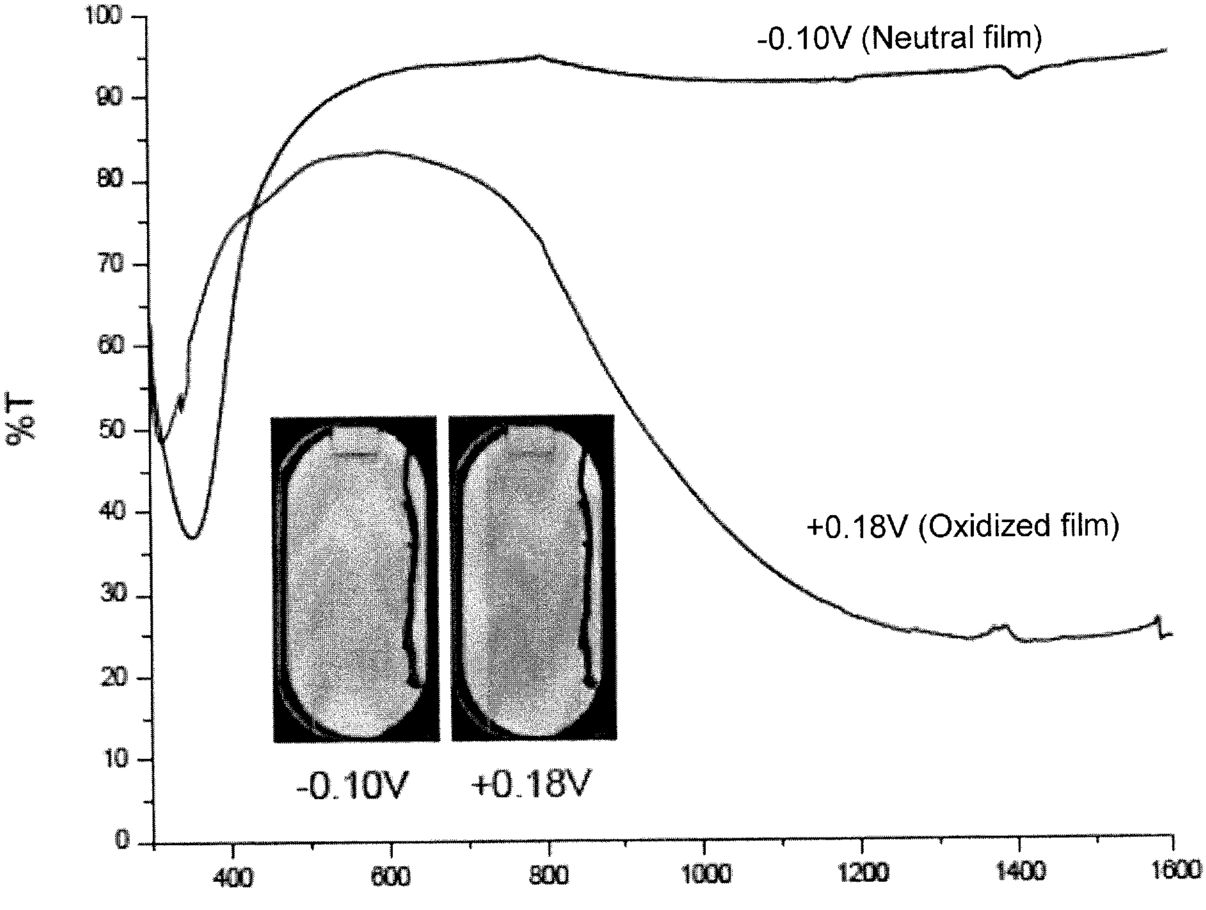
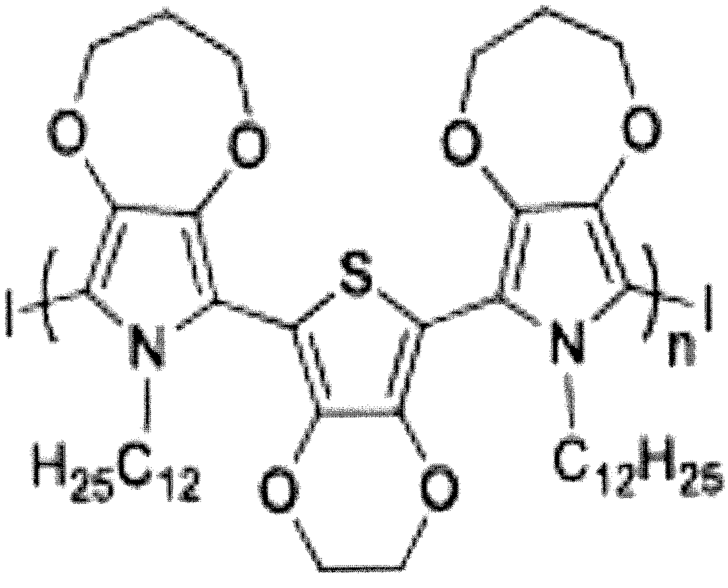

-0.10V (Neutral film)
+0.18V (Oxidized film)
-0.10V
+0.18V
%T
100
90
80
70
60
50
40
30
20
10
0
400
600
800
1000
1200
1400
1600
λ (nm)

Figure 7A


O
O
O
O
S
O
O
N
N
I
I
n
H25C12
C12H25

7a

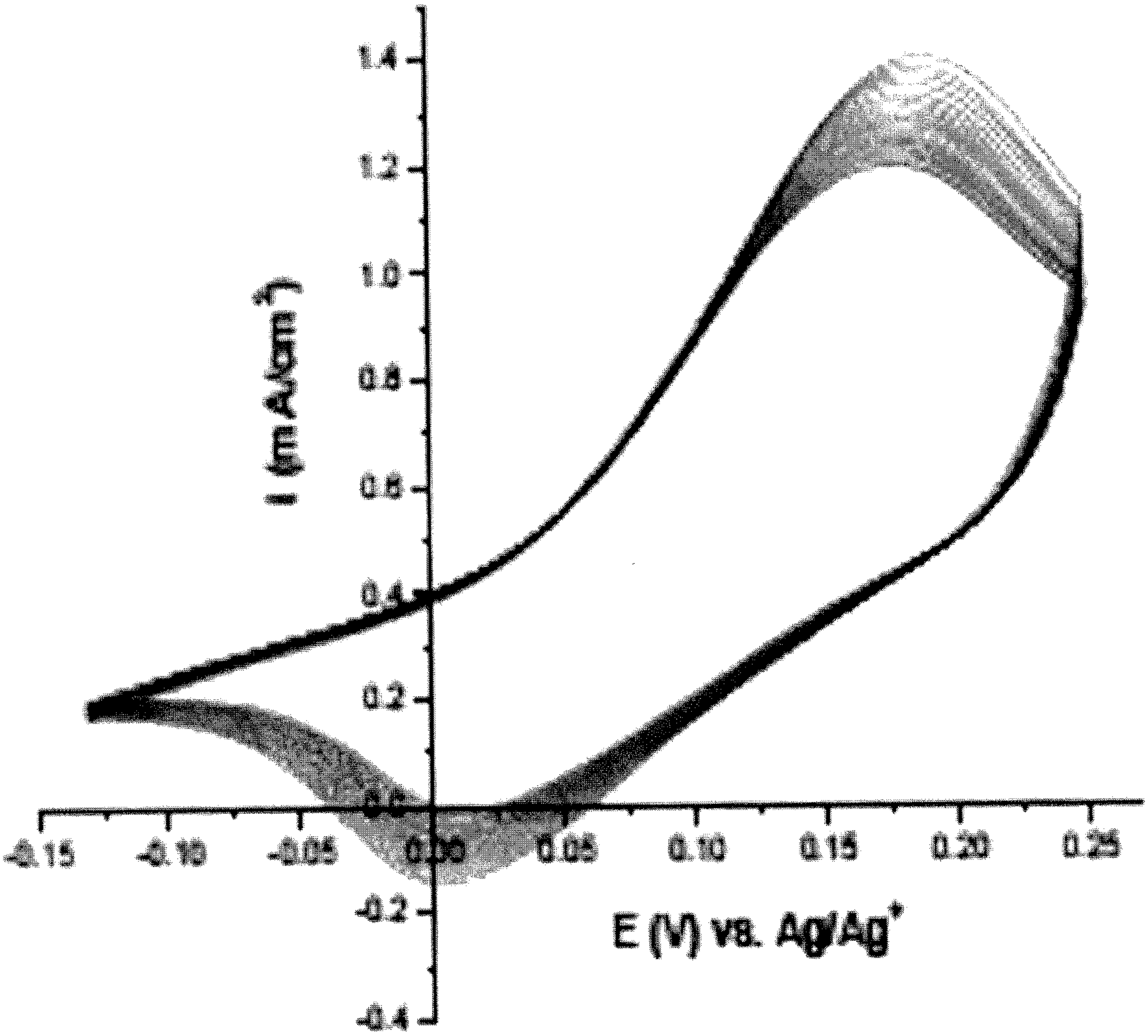

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
I (mA/cm²)
-0.15
-0.10
-0.05
0.00
0.05
0.10
0.15
0.20
0.25
E (V) vs. Ag/Ag⁺

Figure 7B

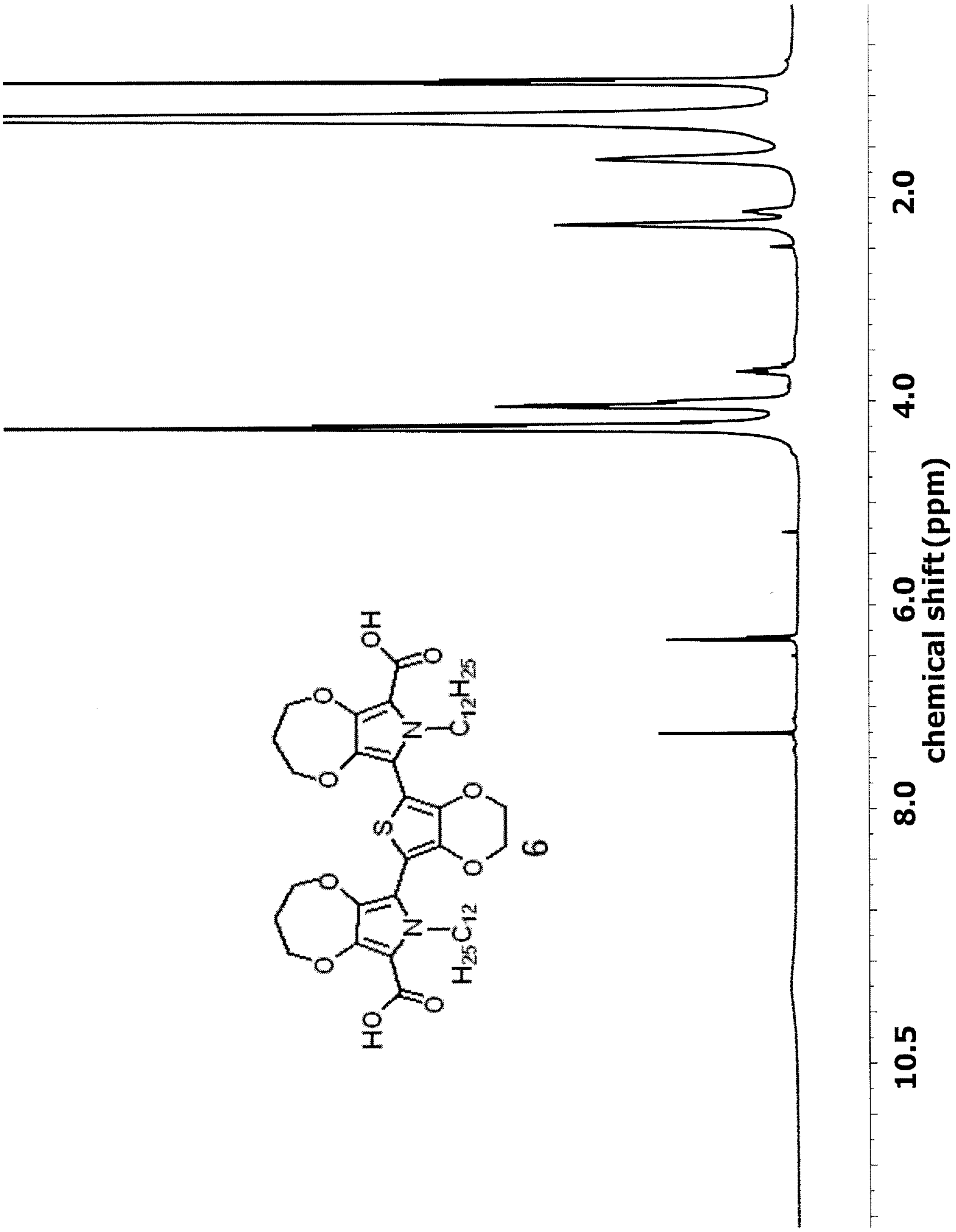


Figure 8

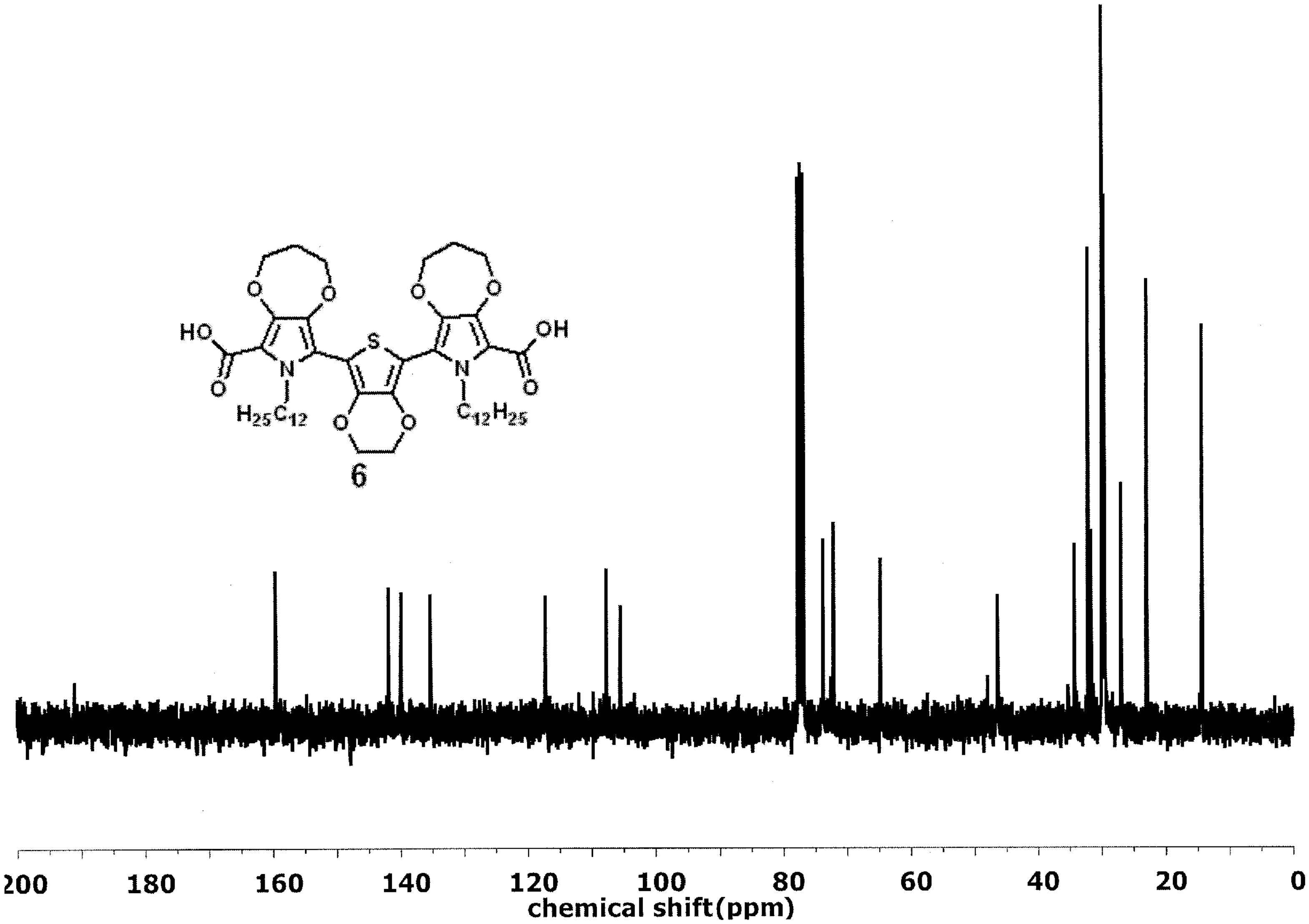
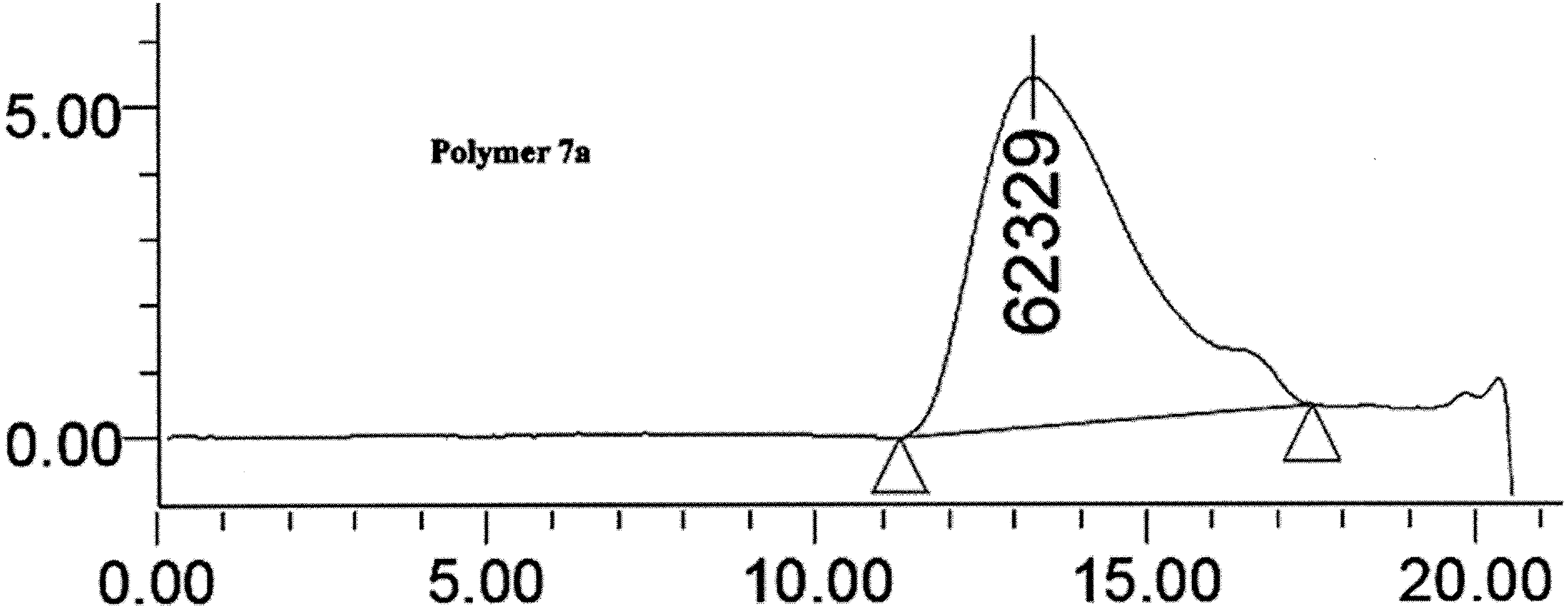

HO
OH
O
S
N
H25C12
C12H25
6
200
180
160
140
120
100
80
60
40
20
0
chemical shift(ppm)

Figure 9



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		22875	58099	62329	99104	133827		2.539835		

Peak Results

	Name	RT	Area	Height	Amount	Units
1	PeakRT14	13.311	873269	5312		

Figure 10

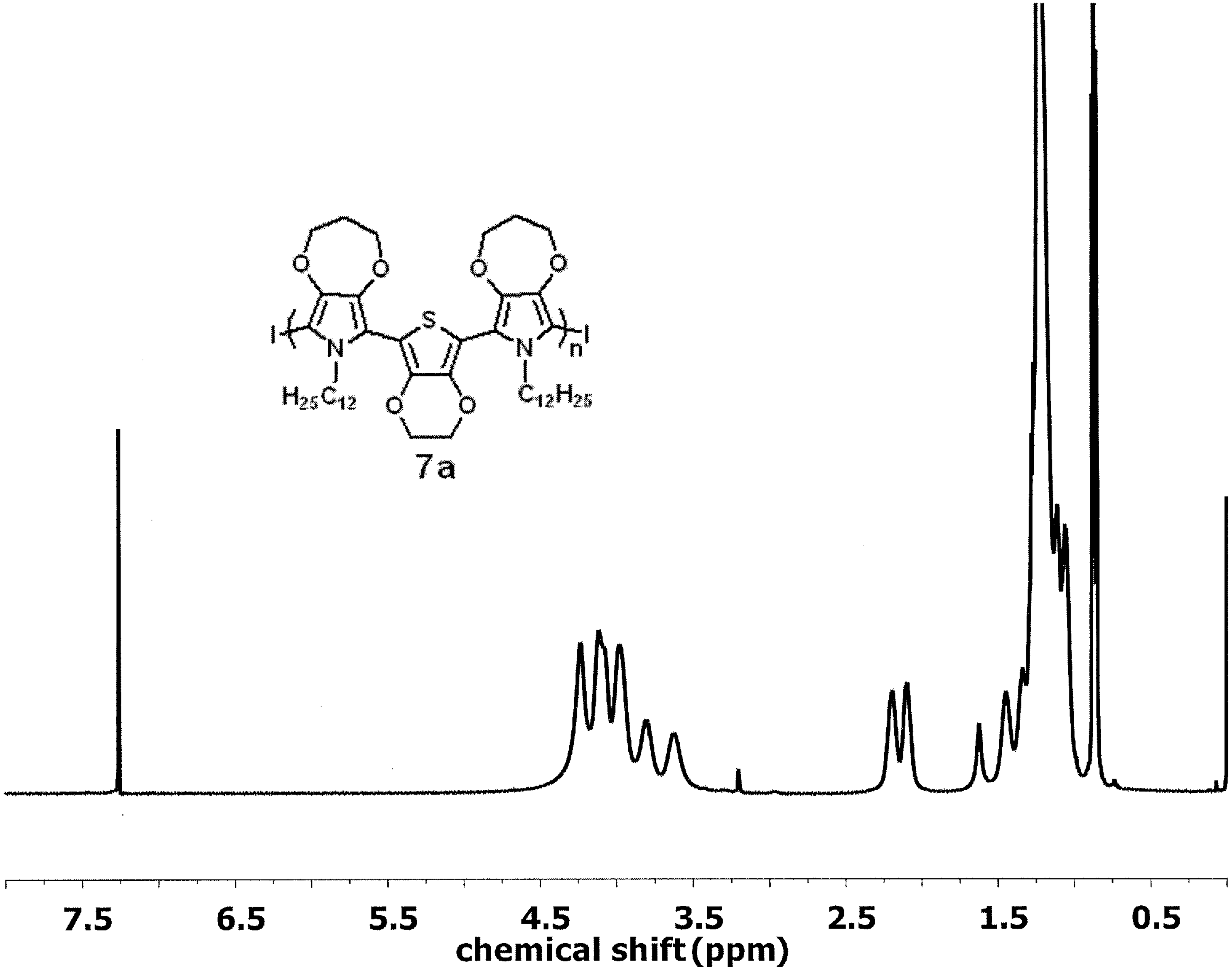

S
N
O
I
n
H25C12
C12H25
7a
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
chemical shift (ppm)

Figure 11

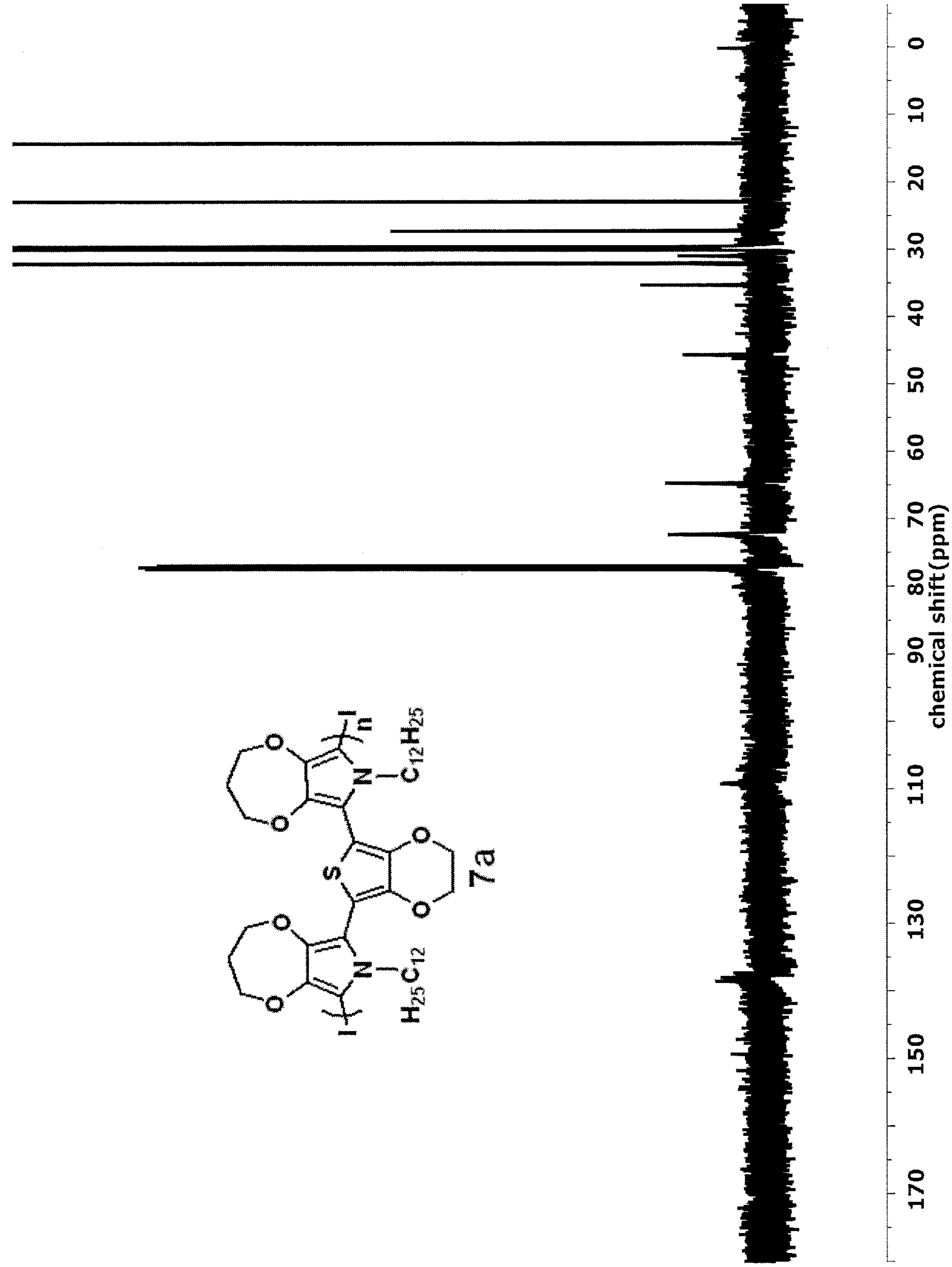
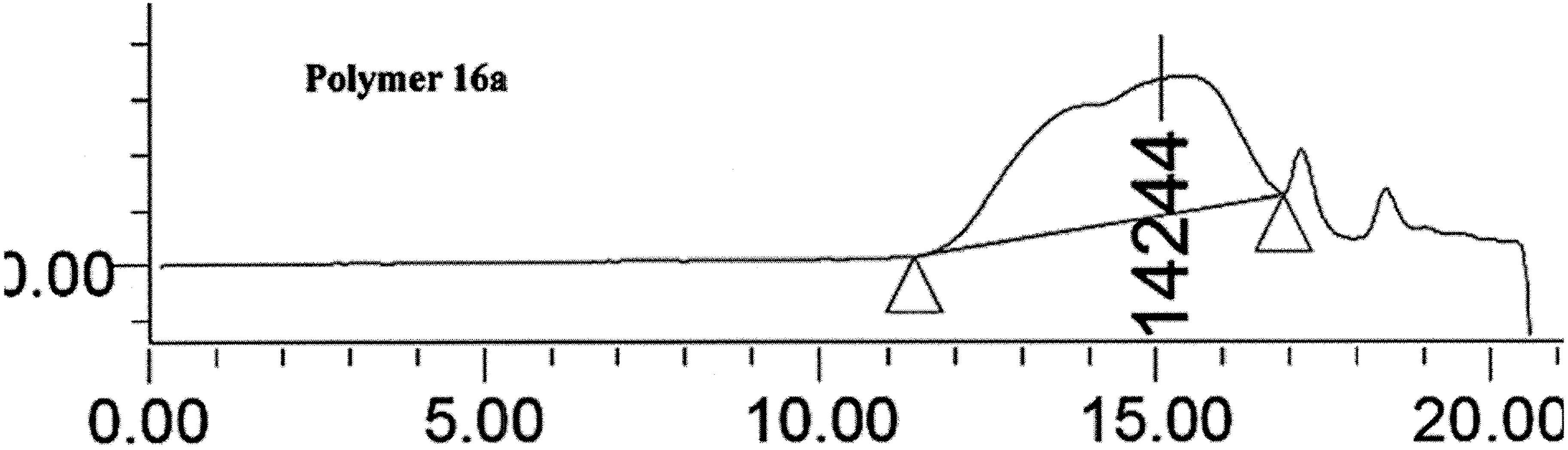

0
10
20
30
40
50
60
70
80
90
110
130
150
170
chemical shift(ppm)
S
O
N
I
n
$C_{12}H_{25}$
$H_{25}C_{12}$
7a

Figure 12



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		15909	35718	14244	72454	109912		2.245145		

Peak Results

	Name	RT	Area	Height	Amount	Units
1	PeakRT15	15.100	497368	2449		

Figure 13

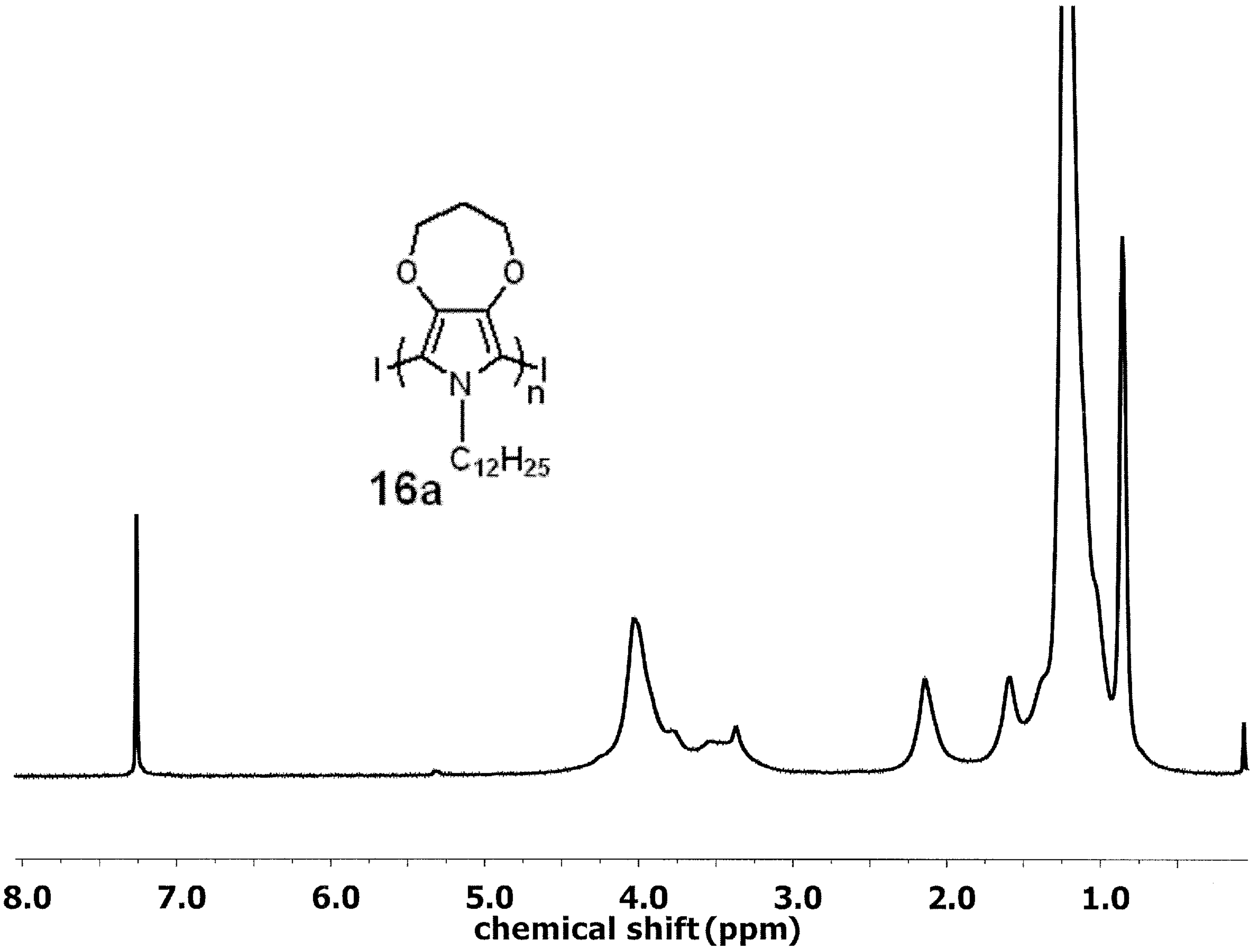


Figure 14

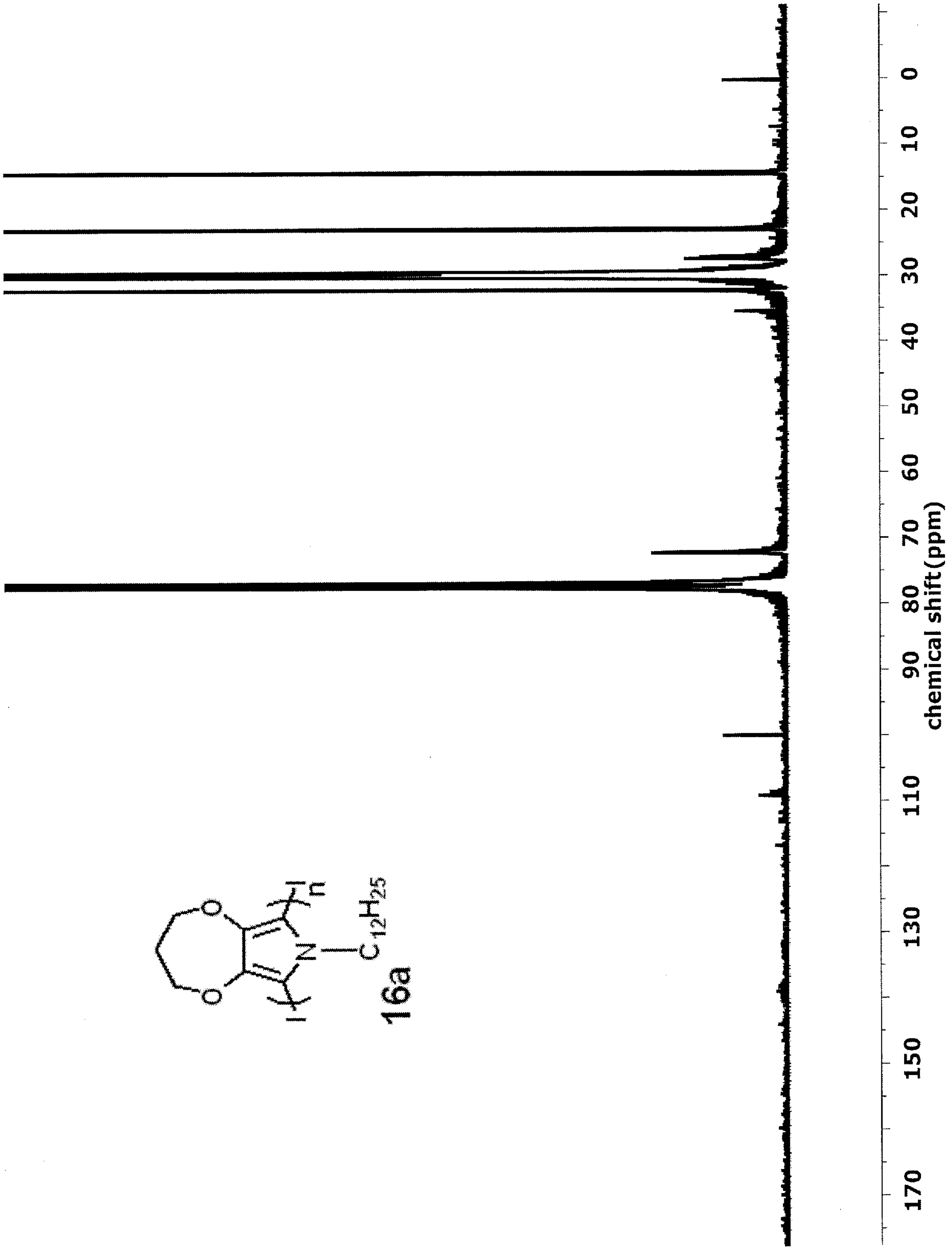

16a
O
O
N
C12H25
n
0
10
20
30
40
50
60
70
80
90
110
130
150
170
chemical shift (ppm)

Figure 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/025830

A. CLASSIFICATION OF SUBJECT MATTER

C08G 61/12(2006.01)i, C08G 73/06(2006.01)i, C08G 75/02(2006.01)i

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)
C07D 345/00; C07D 217/22; C07D 207/36; C07D 491/04; C07D-495/04; C08G 73/06; C08G 75/02; C08G 75/00; C08G 61/00; C08G 61/12; H01L-051/30; H01B-001/12; G02F 1/15; G02F 1/00; G02F 1/15; G02F 1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: ProDOT, polyheterocycle, poly(3,4-dioxypyrrole), polymerization, polythiophenes, polypyrroles, polyfurans, conductor, halogen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007-0270571 A1 (REYNOLDS, JOHN ROBERT et al.) 22 November 2007 See abstract; paragraphs [0011]-[0018]; claims 1-14.	15-16
A		1-14
A	US 2009-0149661 A1 (REYNOLDS, JOHN ROBERT et al.) 11 June 2009 See abstract; paragraphs [0017]-[0019]; claims 1-21.	1-16
A	KR 10-2008-0091253 A (UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC.) 09 October 2008 See abstract; claims 1-31.	1-16
A	US 2010-0298527 A1 (BEAUJUGE, PIERRE MARC et al.) 25 November 2010 See abstract; paragraphs [0006]-[0007] & [0020]-[0024]; claims 1-24 & 26-30; Schemes 2-5.	1-16
A	US 2003-0162958 A1 (REYNOLDS, JOHN R. et al.) 28 August 2003 See abstract; paragraphs [0036]-[0041]; claims 1-10; Table 1.	1-16
A	KR 10-2004-0070181 A (UNIVERSITY OF FLORIDA) 06 August 2004 See abstract; claims 1-11; Figures 17-20.	1-16

☒ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"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
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
23 May 2013 (23.05.2013)

Date of mailing of the international search report
24 May 2013 (24.05.2013)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
KIM, Dong Seok
Telephone No. 82-42-481-8647

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/025830

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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