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(71) Applicant *(for all designated States except US)*: **EMPIRE TECHNOLOGY DEVELOPMENT LLC** [US/US]; 2711 Centerville Road, Suite 400, Wilmington, Delaware 19808 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **BRIZIUS, Glen Leon** [US/US]; 2239 Cadden Road, Augusta, Georgia 30906 (US).

(74) Agents: **WADSWORTH, Curtis C.** et al.; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, Pennsylvania 15219 (US).

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(54) Title: REGIOREGULAR COPOLYMERS AND METHODS FOR MAKING SAME

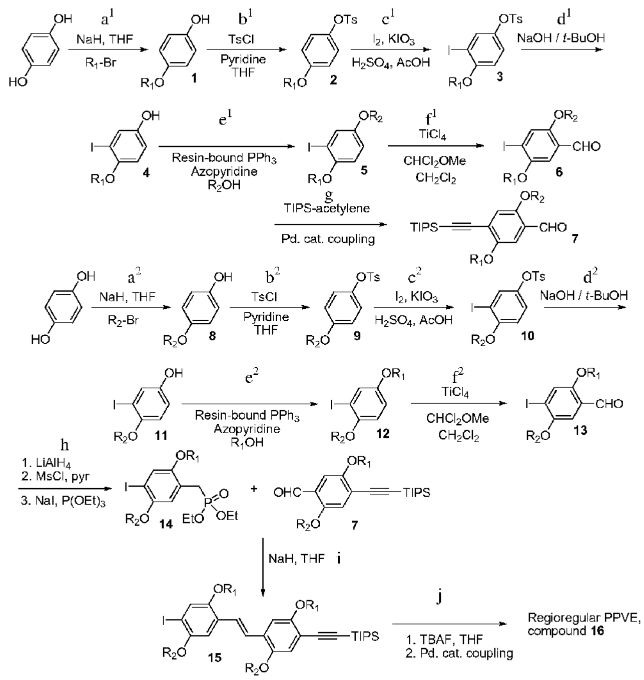

FIG. 1

(57) Abstract: Methods for producing regioregular poly(aryl ethynyl)-poly(aryl vinyl) and monomers for preparing the regioregular poly(aryl ethynyl)-poly(aryl vinyl) polymers are described herein. Regioregular poly(aryl ethynyl)-poly(aryl vinyl) are useful for electronics, among other things.

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REGIOREGULAR COPOLYMERS AND METHODS FOR MAKING SAME

BACKGROUND

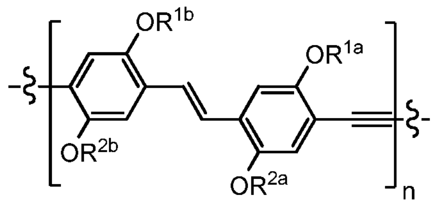
[0001] The classes of polymers known as poly(*p*-phenyleneethynylene)s, or PPEs, and poly(*p*-polyphenylenevinylene)s, or PPVs, have found uses as active layers in light-emitting diodes, “plastic lasers,” light emitting-electrochemical cells, thin film transistors, and chemical sensors. Hybrid polyphenylenevinylene-ethynylenes copolymers, or “PPVEs,” having strictly alternating PPE and PPV monomeric units combine the physical (phase, thermal) behaviour of the PPEs/PPVs with a new class of optical properties, including enhanced electron affinity. This makes PPVEs incredibly promising candidates for use in transistors and other solid-state electronic devices. Their unique electronics can be easily tuned *via* the side chains, while retaining the well-understood solid-state phase behaviour, X-ray diffraction, and the like of the PPEs. Such PPVE polymers have been used for their charge carrier mobility, especially in anthracene-PPVE copolymers, electroluminescent properties, photovoltaic properties for use in solar cells, and as the active component in thin film field effect transistors.

[0002] Work on poly(thiophene)s has shown that the identity and relative position of side chains along a conjugated polymer backbone has a large impact on the properties of the resulting polymer. Normal polymerization methods incorporate all possible combinations into the backbone, producing an inherently regiorandom polymer. There are steric and (in some cases) electronic “clashes” between side chains which “point” towards each other, twisting the backbone out of planarity with corresponding effects on the effective conjugation length and overall polymer crystallinity. This is of great importance, not only for the poly(thiophene)s but for any rigid-rod conjugated polymer that experiences a similar occurrence.

[0003] Regioregular materials have higher crystallinity, red-shifted absorptions in the optical region, a greater conductivity, and (usually) a smaller band-gap compared to the regiorandom versions of the same polymer. This has direct and powerful implications on the use of these materials for electronic applications. These effects have been studied in poly(1,4-phenylenevinylene)s and poly(1,4-phenyleneethynylene)s, but not for PPVEs due primarily to a lack of a valid synthetic route to regioregular PPVEs.

SUMMARY

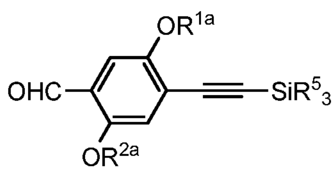
[0004] Embodiments of the invention are generally directed to methods for preparing regioregular copolymers, monomeric units useful in such methods, and methods for preparing these monomeric units. For example, some embodiments include methods for making regioregular aryl ethynyl-aryl vinyl copolymers that include a compound of Formula IV:



IV

wherein each R^{1a}, R^{1b}, R^{2a}, and R^{2b}, independently, is C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and n is an integer of 2 or more.

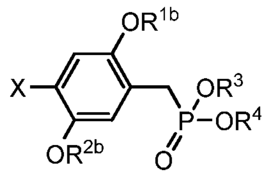
[0005] Other embodiments include compounds having the general Formula I:



I

wherein each R^{1a} and R^{2a} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and each R^5 is, independently, C_1-C_{20} alkyl. Further embodiments include methods for making the compounds of Formula I, and methods that use such compounds for the production of regioregular aryl ethynyl-aryl vinyl copolymers.

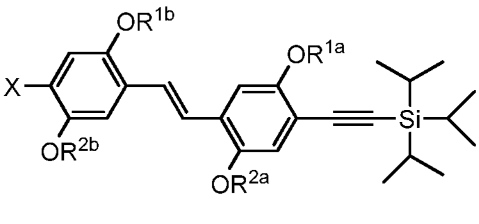
[0006] Still other embodiments include compounds having the general Formula II:



II

wherein each R^{1b} and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; each R^3 and R^4 is, independently, C_1-C_{20} alkyl; and X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). Further embodiments include methods for making the compounds of Formula II, and methods that use such compounds for the production of regioregular copolymers.

[0007] Yet other embodiments are directed to compounds having the general Formula III:



III

wherein each R^{1a}, R^{1b}, R^{2a}, and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; and X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). Further embodiments include methods for making the compounds of Formula III, and methods that use such compounds for the production of regioregular copolymers.

Additional embodiments include methods for making compounds of general Formula III from compounds of general Formulae I and II.

BRIEF DESCRIPTION OF THE FIGURES

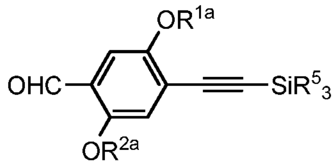
[0008] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be utilized and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0009] **FIG. 1** is a schematic of a chemical synthesis corresponding to the synthesis scheme defined herein.

DETAILED DESCRIPTION

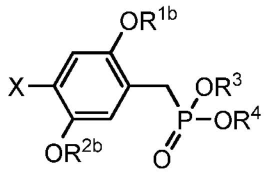
[0010] Various embodiments are directed to monomeric units that can be used in the production of polymers as well as methods for making these monomers. Further embodiments are directed to polymers created using these monomeric units and methods for making such polymers. The monomeric units, or monomers, can be incorporated into any polymer or type of polymer known in the art including various thermoplastic and thermoset resins, and in particular embodiments, the monomers of the invention can be incorporated into regioregular copolymers.

[0011] The monomeric units of various embodiments generally include at least one aromatic moiety. For example, in some embodiments, the monomeric unit may be a silylalkynyl dialkoxyl arylaldehyde such as, but not limited to, a compound of general Formula I:



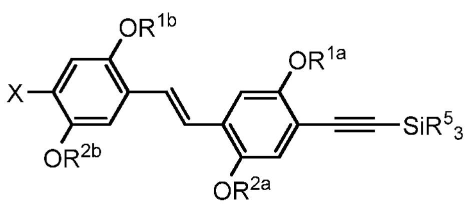
I

[0012] where each R^{1a} and R^{2a} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and each R^5 can be C_1-C_{20} alkyl. In other embodiments, the monomeric unit may be a X-substituted dialkoxyl arylphosphonate such as, but not limited to, a compound of general Formula II:



II

where each R^{1b} and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; each R^3 and R^4 is, independently, C_1-C_{20} alkyl; and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). In still other embodiments, the monomeric unit may be a X-substituted silylalkynyl diarylethene such as, but not limited to, a compound of general Formula III:



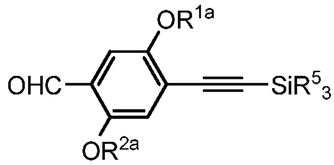
III

where each R^{1a}, R^{1b}, R^{2a}, and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, R^5 can be C_1-C_{20} alkyl, and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate

($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). In each of the embodiments, described above, R^{1a} and R^{1b} can be the same, R^{2a} and R^{2b} can be the same, or R^{1a} and R^{1b} can be the same and R^{2a} and R^{2b} can be the same, and in some embodiments, R^{1a}, R^{1b}, R^{2a}, and R^{2b} can each be different, or various combinations of R^{1a}, R^{1b}, R^{2a}, and R^{2b} can be the same or different.

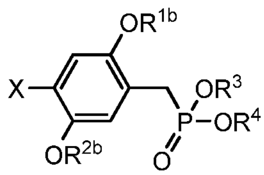
[0013] Without wishing to be bound by theory, the leaving groups X, *e.g.* hydroxide, alkoxide, asataine, iodine, brome, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$)), phosphonate ($P(O)OR^3OR^4$), aldehyde (CHO), and silyl ($\equiv C(SiR_5)_3$) groups associated with the monomeric units exemplified above may allow these monomeric units to be particularly useful for any number of polymerization reactions. Moreover, the arrangement of these leaving groups provides a means for controlling the arrangement of these monomeric units. For example, in certain embodiments, the monomeric units described above, or other compounds having the leaving groups described above may be used in the preparation of regiospecific or regioregular polymers in reactions that are regioselective. A "regioselective reaction" is a chemical reaction in which one direction of bond making or breaking occurs preferentially over all other possible directions. The term "regiospecific" or "regiospecific reaction" as used herein refers to a polymerization reaction that is 100% or nearly 100% regioselective, resulting in a polymer that is exclusively or nearly exclusively composed of one of several possible isomeric products. Generally, regiospecific is defined as a reaction that results in regioselectivity within the limit of detection. For ^1H NMR, the current standard method, about 95% to about 100%, about 97% to about 100%, about 98% to about 100%, or about 99% to about 100% of the bonds in a regiospecific polymer will be of one isomeric product. The isomeric products of regiospecific reactions are referred to as "regioregular polymers."

[0014] In some embodiments, the monomeric units may be used in regioselective or regiospecific reactions that are intended to result in regioregular polymers. For example, particular embodiments are directed to a method for preparing regioregular aryl ethynyl-aryl vinyl copolymers. In general, such methods may include the steps of providing a silylalkynyl dialkoxyl arylaldehyde and a X-substituted dialkoxyl arylphosphonate and contacting the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate under conditions that provide for coupling of the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate to provide a X-substituted silylalkynyl diarylethene. In particular embodiments, the silylalkynyl dialkoxyl arylaldehyde may be a compound of Formula I:



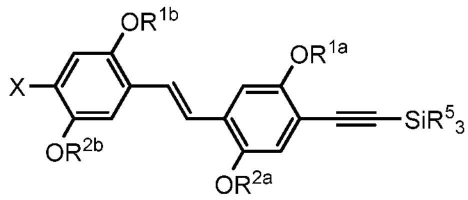
I

where each R^{1a} and R^{2a} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, or C_2-C_{20} alkyne and each R^5 can be C_1-C_{20} alkyl, and in some embodiments, the X-substituted dialkoxyl arylphosphonate comprises a compound of Formula II:



II

where each R^{1b} and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, each R^3 and R^4 can, independently, be C_1-C_{20} alkyl, and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). In certain embodiments, R^{1a} and R^{1b} can be the same and R^{2a} and R^{2b} can be the same. In particular embodiments, contacting the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate under conditions that provide for coupling of the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate may include a Horner-Wadsworth-Emmons coupling. The X-substituted dialkoxyl arylphosphonate may be of any formula and, in some embodiments, may be a compound of Formula III:

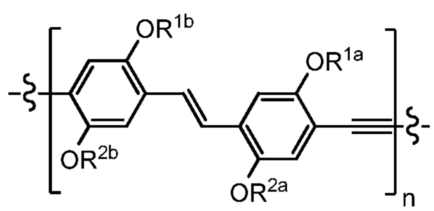


III

where each R^{1a}, R^{1b}, R^{2a}, and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, R^5 can be C_1-C_{20} alkyl, and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).

[0015] In some embodiments, such methods may further include the steps of placing the X-substituted silylalkynyl diarylethene under conditions that allow the silyl moiety to be removed from the X-substituted silylalkynyl diarylethene to provide a X-substituted alkynyl diarylethene and placing the X-substituted alkynyl diarylethene under conditions that allow X-substituted alkynyl diarylethenes to be coupled to provide the regioregular aryl ethynyl-aryl vinyl copolymer. In particular embodiments, the coupling reaction resulting from placing the X-substituted alkynyl diarylethene under conditions that allow the X-substituted alkynyl diarylethenes to be coupled may be a Sonogashira coupling.

[0016] In embodiments, such as those described above, the resulting regioregular copolymer may be a compound of Formula IV:



IV

where each R^{1a}, R^{1b}, R^{2a}, and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, and n can be an integer from 2 or more, or in some embodiments, n may be an integer from 2 to 100. In certain embodiments, R^{1a} and R^{1b} may be the same and R^{2a} and R^{2b} may be the same, and in particular embodiments, the copolymer of Formula IV can be regioregular.

[0017] The method described above may have any number of additional steps, and such additional steps may be carried out in any order. For ease of description, FIG. 1 provides a reaction scheme for the synthesis of various regioregular copolymers encompassed by the invention. Intermediate compounds formed during the synthesis are numbered and individual steps in the synthesis method are identified using letters. As indicated by the superscripts, steps a-f are carried out in the preparation of both monomeric units corresponding to Formulae I and II described above, which are identified in the reaction scheme of FIG. 1 as compounds **7** and **14** respectively.

[0018] In FIG. 1, synthesis of the regioregular aryl ethynyl-aryl vinyl copolymers begins in step a^1, a^2 by providing a *para*-substituted arene **0**, which is exemplified by hydroquinone, and a halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol. These components are combined or "contacted" under conditions that allow the *para*-substituted arene **0** and the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol to react to provide a monoalkoxyl *para*-substituted arene **1**. In some exemplary embodiments, the *para*-substituted arene may be hydroquinone, and in certain embodiments, the monoalkoxyl *para*-substituted arene **1** produced by this step may be a 4-alkoxyphenol. In particular embodiments, the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, or C_2-C_{20} alkyne used in step a^1 may be different from the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, or C_2-C_{20} alkyne used in step a^2 such that R^{1a} of intermediate **1** may be different from R^{2b} of intermediate **8**. In other embodiments, the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene,

C_2-C_{20} alkyne, or alkylene glycol used in step a^1, a^2 may be the same such that intermediates **1** and **8** will be the same. Steps a^1-f^1 and a^2-f^2 are generally carried out separately; however, in certain embodiments in which R^{1a} and R^{2b} are the same, steps a^1-f^1 and a^2-f^2 may be carried out simultaneously in the same reaction vessel.

[0019] Attachment of one side chain to the *para*-substituted arene **0** is generally achieved by nucleophilic substitution (S_N2), which typically produces about 60% to about 70% yield of the monoalkoxyl *para*-substituted hydroxyarene **1** product. Without wishing to be bound by theory, based on the different solubilities of *para*-substituted arene **0**, the monoalkoxyl para-substituted hydroxyarene **1**, and di-substituted by-products, the monoalkoxyl *para*-substituted hydroxyarene **1** can be easily purified by recrystallization. The size and nature of R^1 and/or R^2 can vary among embodiments, and may depend on the intended end use of the polymer. In embodiments in which R^1 and/or R^2 are long alkyl chains, recrystallization may result in a white solid.

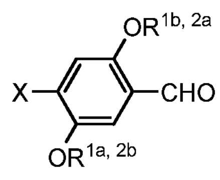
[0020] In step b^1, b^2, a protecting group may be introduced onto the monoalkoxyl *para*-substituted hydroxyarene **1, 8,** at the remaining hydroxyl in a step that includes contacting a protecting group containing compound and the monoalkoxyl *para*-substituted hydroxyarene **1, 8** under conditions that allow the protecting group containing compound and the monoalkoxyl *para*-substituted hydroxyarene **1, 8,** to react to provide the protected monoalkoxyl *para*-substituted arene **2, 9**. The protecting group containing compound may be any known protecting group containing compound, and in some embodiments, the protecting group may be bulky and/or electron withdrawing. For example, in various embodiments, the protecting group containing compound may be acetyl, benzoyl, benzyl, β-methoxyethoxymethyl ether, dimethoxytrityl, [bis-(4-methoxyphenyl)phenylmethyl], methoxymethyl ether, methoxytrityl [(4-methoxyphenyl)diphenylmethyl], *p*-methoxybenzyl ether, methylthiomethyl ether, pivaloyl, tetrahydropyranyl, trityl triphenylmethyl, silyl ether, trimethylsilyl ether, *tert*-butyldimethylsilyl ether, tri-*iso*-propylsilyloxymethyl ether, tri-*iso*-propylsilyl ether, ethoxyethyl ether, carbobenzyloxy, *p*-methoxybenzyl carbonyl, *tert*-butyloxycarbonyl, 9-fluorenylmethyloxycarbonyl, carbamate, *p*-methoxybenzyl, 3,4-dimethoxybenzyl, *p*-methoxyphenyl, tosyl, sulfonamide, and the like and combinations thereof. In particular embodiments, the protecting group may be a tosyl, and in certain embodiments, protected monoalkoxyl *para*-substituted arene **2, 9,** may be 4-(alkoxy)phenyl 4-protecting group, such as the tosylate (Ts) containing compound, 4-(alkoxy)phenyl 4-methylbenzensulfonate, in FIG. 1. In embodiments, in which the protecting group is a tosylate group, the addition of the protecting group may be carried out by combining the monoalkoxyl *para*-substituted arene **1, 8,** with tosyl chloride (TsCl) in pyridine at room temperature. Without wishing to be bound by theory, a tosylate protecting group is stable to acid, readily cleaved by base, but also presents a steric barrier towards electrophilic aromatic substitution at the a-substituents on the benzene ring of the monoalkoxyl *para*-substituted arene **1, 8**.

[0021] In various embodiments, a leaving group (X) may be introduced onto the arene of the monoalkoxyl *para*-substituted arene **2, 9,** at a carbon adjacent to the alkoxy substituent, step c^1, c^2. In various embodiments, the leaving group X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$) In exemplary embodiments, the leaving group (X) may consist of iodine. Thus, the method of embodiments may include the step of placing the protected monoalkoxyl arene **2, 9,** under conditions that allow the addition of a leaving group (X) to the protected monoalkoxyl arene **2, 9,** to provide the protected X-substituted monoalkoxyl arene **3, 10**. In certain embodiments, the protected X-substituted monoalkoxyl arene **3, 10,** may be 3-halogen 4-alkoxyphenyl 1-protecting group, and in some embodiments, the protected X-substituted monoalkoxyl arene **3, 10,** may be 3-iodo-4-(alkoxy)phenyl 1-methylbenzensulfonate, as illustrated in FIG. 1. Without wishing to be bound by theory, the presence of the protecting group opposite the alkoxyl group, i.e., at a *para* position, may reduce or eliminate the possibility of a leaving group (X) being introduced onto a carbon adjacent to the protecting group. In some embodiments, introducing a leaving group (X) onto the monoalkoxyl arene **2, 9**, can be carried out by oxidative iodination in acidic medium which yields the desired monoiodinated monoalkoxyl arene **3, 10** in good yield.

[0022] In various embodiments, the protecting group may be removed after the addition of a leaving group (X) has been carried out. For example, in some embodiments, the method may include the step of placing the protected X-substituted monoalkoxyl *para*-substituted arene **3, 10,** under conditions that allow a protecting group to be removed from the protected X-substituted monoalkoxyl arene **3, 10,** to provide the unprotected X-substituted monoalkoxyl hydroxyarene **4, 11**. In particular embodiments where the leaving group (X) consists of iodine, a tosylate group may be removed by a mixture of aqueous sodium hydroxide (NaOH) and *t*-butanol at reflux, and acidic workup can yield free iodophenol.

[0023] A second alkyl, alkene, or alkyne R^{2a}, R^{1b} can then be introduced onto the hydroxyl remaining after the protecting group has been removed. In some embodiments, the method may include the step e^1, e^2 of contacting a hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, and the unprotected X-substituted monoalkoxyl hydroxyarene **4, 11,** under conditions that allow the hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene gylcol and the unprotected X-substituted monoalkoxyl hydroxyarene **4, 11,** to react to provide the unprotected X-substituted dialkoxyll arene **5, 12**. In various embodiments, the alkyl, alkene, alkyne, or alkylene glycol R^{2a}, R^{1b} introduced in step e^1, e^2 may be the same as the alkyl, alkene, alkyne, or alkylene glycol R^{1a}, R^{2b} introduced onto the *para*-substituted arene **0** in step a^1, a^2. In certain embodiments, the alkyl, alkene, alkyne, or alkylene glycol R^{2a} introduced in step e^1 may be the same alkyl, alkene, or alkyne R^{2b} introduced in step a^2, and the alkyl, alkene, alkyne, or alkylene glycol R^{1b} introduced in step e^2 may be the same alkyl, alkene, alkyne, or alkylene glycol R^{1a} introduced in step a^1. Thus, in some embodiments, the hydroxylated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol may include different C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol moieties. In particular embodiments, the step of contacting in steps e^1 and e^2 may include a Mitsunobu coupling, and in some embodiments, the Mitsunobu coupling can be carried out using resin bound triphenylphosphine (PPh_3). A Mitsunobu coupling is then used which may utilize modified conditions, including resin-bound PPh_3 (to enable easy purification of the coupled product / regeneration of the resin) as well as azopyridine instead of diethyl azodicarboxylate (DEAD), which can be regenerated and reused. In particular embodiments, the second side chain attached in this step can be non-identical to R^1 and can be tailored to meet the final demands of the polymer.

[0024] The methods of various embodiments may further include the step of introducing an aldehyde-containing substituent onto the unprotected X-substituted dialkoxyl arene **5, 12**. Such steps can be carried out by contacting a C_1-C_6 alkoxy C_1-C_6 dihaloalkyl and the unprotected X-substituted dialkoxyl arene **5, 12** under conditions that allow the C_1-C_6 alkoxy C_1-C_6 dihaloalkyl and the unprotected X-substituted dialkoxyl arene **5, 12** to react to provide the X-substituted dialkoxyl arylaldehyde **6, 13**. In certain embodiments, the X-substituted dialkoxyl arylaldehyde **6, 13** may be a compound of Formula V:



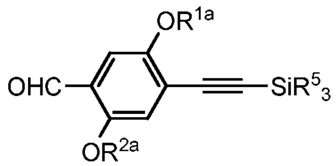
V

where each R^{1a}, R^{1b}, R^{2a}, and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$). Without wishing to be bound by theory, the directing effects of the R^{2a} or R^{1b} and R^{1a}, or R^{2b} and the leaving group (X) on the benzene cause the aldehyde (CHO) to be positioned opposite, i.e., *para*, to the leaving group (X) under various reaction conditions. For example, in particular embodiments, when the X-substituted dialkoxyl arene **5, 12** may be exposed to a mixture of $TiCl_4/CHCl_2OCH_3$ dissolved in dichloromethane (CH_2Cl_2) at low temperatures (-10°C, ice-salt bath) to provide the X-substituted dialkoxyl arylaldehyde **6, 13** having the aldehyde in the proper position.

[0025] As discussed above, the synthetic route for silylalkynyl dialkoxyl arylaldehyde **7** monomer and the X-substituted dialkoxyl arylphosphonate **14** are similar. However, in certain embodiments, the side chain $R^{1a,2b}$ may be first attached to the *para*-substituted arene **0** first instead of $R^{2a,1b}$ to ensure that in the final monomer, similar side chains are arranged in the proper orientation with respect to each other and do not become mismatched. This provides the regioregular polymer. Thus steps leading up to intermediate **6** are the same as the steps leading to intermediate **13**, with the exception that now the placement of the two side chains are switched.

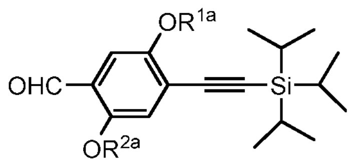
[0026] The preparation of the silyl-containing monomer of Formula I, intermediate **7** in FIG. 1, may proceed by introducing a silyl containing group onto the X-substituted dialkoxyl arylaldehyde **6**, step g. For example, in some embodiments, the method may include contacting a silyl-alkynyl and the X-substituted dialkoxyl arylaldehyde **6** under conditions that allow the silyl-alkynyl and X-substituted dialkoxyl arylaldehyde **6** to react to provide the silylalkynyl dialkoxyl arylaldehyde **7**. The silyl-alkynyl may be any silyl alkynyl group known in the art including, but not limited to, trimethylsilyl acetylene, *tert*-

butyldimethylsilyl acetylene, tri-*iso*-propylsilyloxymethyl acetylene, or tri-*iso*-propylsilyl acetylene, and in certain embodiments, the silyl-alkynyl may be tri-*iso*-propylsilyl acetylene, *i.e.*, TIPS, as exemplified in FIG. 1. Step g, may result in a compound of Formula I:



I

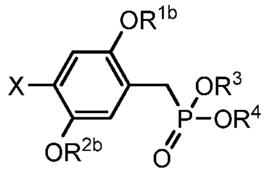
where each R^{1a} and R^{2a} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and each R^5 can be C_1-C_{20} alkyl. In particular embodiments the monomeric unit **7** resulting from step g may be a compound of general Formula Ia:



Ia

where R^{1a} and R^{2a} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol. In particular embodiments, the X-substituted dialkoxyl arylaldehyde **6** can be coupled to one equivalent of silyl containing compound such as TIPS-acetylene (TIPS = tri-*iso*-propyl silyl) under palladium-catalyzed coupling conditions to produce a protected alkyne, silylalkynyl dialkoxyl arylaldehyde **7**. The reaction proceeds quantitatively, and the TIPS-alkyne group is stable to a wide variety of reaction conditions and can be easily removed to give the bare alkyne.

[0027] The phosphonate containing monomer of Formula II, intermediate **14** in FIG. 1, can be produced by introducing a phosphonate group into the X-substituted dialkoxyl arylaldehyde **13**, step h. In some embodiments, the method may include the step of contacting a phosphonate containing compound and the X-substituted dialkoxyl arylaldehyde **13** under conditions that allow the phosphonate containing compound and the X-substituted dialkoxyl arylaldehyde **13** to react to provide the X-substituted dialkoxyl arylphosphonate monomer **14**. Step h may generally result in a X-substituted dialkoxyl arylphosphonate **14** having a structure of Formula II:



II

where each R^{1b} and R^{2b} can, independently, be C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol, each R^3 and R^4 can, independently, be C_1-C_{20} alkyl, and X can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).

[0028] In particular embodiments, contacting the phosphonate-containing compound and the X-substituted dialkoxyl arylaldehyde **13** may include various additional steps such as, for example, placing the X-substituted dialkoxyl arylaldehyde **13** under conditions that allow the X-substituted dialkoxyl arylaldehyde **13** to be reduced to provide a X-substituted dialkoxyl arylmethanol; combining the X-substituted dialkoxyl arylmethanol with a leaving group containing compound; contacting the leaving group containing compound with the X-substituted dialkoxyl arylmethanol under conditions that allow the leaving group containing compound with the X-substituted dialkoxyl arylmethanol to provide a X-substituted dialkoxyl arylmethyl-leaving group; contacting the X-substituted dialkoxyl arylmethyl-leaving group with a phosphite containing compound under conditions that allow the X-substituted dialkoxyl arylmethyl-leaving group with a phosphite containing compound to react; and allowing an Arbuzov rearrangement to occur to provide the X-substituted dialkoxyl arylphosphonate **14** monomer. In various such embodiments, the leaving group can be, for example, hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate ($CF_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$), or the like and combinations thereof, and in particular embodiments, the leaving group may be mesylate ($CH_3SO_3^-$). In some embodiments, the Arbusov rearrangement can be carried out with a metal halide catalyst such as, for example, sodium iodide (NaI). This reaction can be done neat in triethylphosphite to drive the equilibrium towards formation of products and to reduce hazardous waste streams; residual leftover "solvent" can be vacuum stripped away and used for another batch.

[0029] Following preparation of the silyl containing monomeric unit, intermediate 7, and the phosphonate containing monomeric unit, intermediate **14**, can be coupled to produce a X-substituted silylalkynyl diarylethene **15**. In such embodiments, the method may include the steps of combining the silylalkynyl arylaldehyde **7** and the X-substituted arylphosphonate **14** and contacting the silylalkynyl arylaldehyde **7** and the X-substituted arylphosphonate **14** under conditions that allow the silylalkynyl arylaldehyde **7** and the X-substituted arylphosphonate **14** to react to create a X-substituted silylalkynyl diarylethene **15**. In particular embodiments, the conditions under which the silylalkynyl arylaldehyde **7** and the X-substituted arylphosphonate **14** are combined to reactcomprises a Horner-Wadsworth-Emmons coupling. In some embodiments, the Horner-Wadsworth-Emmons coupling between intermediates **7** and **14** can be carried out using sodium hydride (NaH) in tetrahydrofuran (THF), and produces intermediate **15** in quantitative yield. Notably, the Horner-Wadsworth-Emmons coupling typically forms alkenes in exclusively the *trans* configuration.

[0030] Finally, a regioregular aryl ethynyl-aryl vinyl copolymer **16** can be produced by coupling X-substituted silylalkynyl diarylethenes **15**. In certain embodiments, the coupling X-substituted silylalkynyl diarylethenes **15** may be carried out by placing the X-substituted silylalkynyl diarylethene **15** under conditions that allow the silyl to be removed to provide X-substituted alkynyl diarylethene **15** and contacting the X-substituted diarylethene alkynyl diarylethene **15** under conditions that allow the X-substituted diarylethene alkynyl diarylethene **15** to be coupled to provide a regioregular poly(aryl ethynyl)-poly(aryl vinyl) **16**. In certain embodiments, the coupling of X-substituted alkynyl diarylethene diarylethene **15** can be carried out under conditions that allow the X-substituted diarylethene alkynyl diarylethene **15** to be coupled by a Sonogashira coupling. In particular embodiments, coupling X-substituted silylalkynyl diarylethenes **15** may be carried out with one equivalent of tetra-*n*-butyl ammonium fluoride (TBAF) in THF at room temperature. The fluoride ions produced under these conditions allow for the removal of the alkyne protecting group leaving a base alkyne and gives the monoethynyl monoiodo monomer. The Sonogashira coupling may generally avoid homo-coupled byproducts between two alkyne groups, which would introduce regiorandomness *via* diyne defects and results in the regioregular poly(aryl ethynyl)-poly(aryl vinyl) **16**. The Sonogashira couplings can result in regioregular poly(aryl ethynyl)-poly(aryl vinyl) **16** having about 100 repeating units, which is well above the threshold of saturation for optical properties in these polymers.

[0031] The reaction described above allows for side chains having a wide variety of properties that will allow for the production of a wide variety of polymers having various characteristics of a fully regioregular polymer.

EXAMPLES

EXAMPLE 1: Synthesis of 2-methoxy-5-ethoxy-4-((tri-*iso*-propylsilyl)ethynyl)benzaldehyde

[0032] Hydroquinone can be added to a solution of sodium hydride (NaH) dissolved in tetrahydrofuran (THF) and combined with ethyl bromide yielding *para*-ethoxyphenol. The *para*-ethoxyphenol can be extracted and added to a solution of tosyl chloride (TsCl) dissolved in pyridine and tetrahydrofuran (THF) at room temperature, yielding *para*-ethoxytosyloxybenzene. The *para*-ethoxytosyloxybenzene can be extracted and added to a solution of diatomic iodine (I_2) and potassium iodide trioxide (KIO_3) dissolved in sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH) yielding 4-ethoxy-3-iodo-1-

tosyloxybenzene. The 4-ethoxy-3-iodo-1-tosyloxybenzene is extracted and added to a solution of aqueous sodium hydroxide (NaOH) and *tert*-butanol, removing the tosylate protecting group and yielding 4-ethoxy-3-iodophenol. The 4-ethoxy-3-iodophenol can be extracted and exposed to resin-bound triphenyphosphine (PPh_3) in a solution of azopyridine and methanol (CH_3OH) in a salt bath at 0 °C, yielding 4-ethoxy-3-iodomethoxybenzene. The 4-ethoxy-3-iodomethoxybenzene can be extracted and added to a solution of titanium tetrachloride ($TiCl_4$) and 1,1-dichlorodimethylether ($CHCl_2OCH_3$) dissolved in dichloromethane (CH_2Cl_2) in a salt bath at -10 °C, yielding 2-methoxy-4-iodo-5-ethoxybenzaldehyde. The 2-methoxy-4-iodo-5-ethoxybenzaldehyde can be extracted and half of the yield can be added to tri-*iso*-propylsilylacetylene (TIPS-acetylene) in an amine solvent such as triethylamine, diethylamine, piperidine, or di-*iso*-propylethylamine. This mixture can be passed over a palladium (Pd) catalyst bed, yielding 2-methoxy-5-ethoxy-4-((tri-*iso*-propylsilyl)ethynyl)benzaldehyde.

EXAMPLE 2: Synthesis of diethyl 2-ethoxy-4-iodo-5-methoxybenzylphosphonate

[0033] Hydroquinone can be added to a solution of sodium hydride (NaH) dissolved in tetrahydrofuran (THF) and combined with methyl bromide yielding *para*-methoxyphenol. The *para*-methoxyphenol can be extracted and added to a solution of tosyl chloride (TsCl) dissolved in pyridine and tetrahydrofuran (THF) at room temperature, yielding *para*-methoxytosyloxybenzene. The *para*-methoxytosyloxybenzene can be extracted and added to a solution of diatomic iodine (I_2) and potassium iodide trioxide (KIO_3) dissolved in sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH) yielding 4-methoxy-3-iodo-1-tosyloxybenzene. The 4-methoxy-3-iodo-1-tosyloxybenzene can be extracted and added to a solution of aqueous sodium hydroxide (NaOH) and *tert*-butanol, removing the tosylate protecting group and yielding 4-methoxy-3-iodophenol. The 4-methoxy-3-iodophenol can be extracted and exposed to resin-bound triphenyphosphine (PPh_3) in a solution of azopyridine and ethanol (CH_3CH_2OH) in a salt bath at 0 °C, yielding 4-ethoxy-2-iodomethoxybenzene. The 4-ethoxy-2-iodomethoxybenzene can be extracted and added to a solution of titanium tetrachloride ($TiCl_4$) and 1,1-dichlorodimethylether ($CHCl_2OCH_3$) dissolved in dichloromethane (CH_2Cl_2) in a salt bath at -10 °C, yielding 2-ethoxy-4-iodo-5-methoxybenzaldehyde. The 2-ethoxy-4-iodo-5-methoxybenzaldehyde can be added to lithium aluminum hydride ($LiAlH_4$) and methanesulfonyl chloride (CH_3SO_2Cl) dissolved in pyridine, and then sodium iodide (NaI) and triethyl phosphite ($P(OCH_2CH_3)_3$) can be added to the reaction mixture, yielding diethyl 2-ethoxy-4-iodo-5-methoxybenzylphosphonate.

EXAMPLE 3: <u>Synthesis of (*E*)-((4-(2-ethoxy-4-iodo-5-methoxystyryl)-(2-ethoxy-5-methylphenyl)ethynyl)tri-*iso*-propylsilane</u>

[0034] The 2-methoxy-5-ethoxy-4-((tri-*iso*-propylsilyl)ethynyl)benzaldehyde and diethyl 2-ethoxy-4-iodo-5-methoxybenzylphosphonate can be added to a solution containing sodium hydride (NaH) dissolved in tetrahydrofuran (THF), yielding (*E*)-((4-(2-ethoxy-4-iodo-5-methoxystyryl)-(2-ethoxy-5-methylphenyl)ethynyl)tri-*iso*-propylsilane.

[0035] The (*E*)-((4-(2-ethoxy-4-iodo-5-methoxystyryl)-(2-ethoxy-5-methylphenyl)ethynyl)tri-*iso*-propylsilane can be extracted and added to a solution of tetra-*n*-butylammonium fluoride (TBAF) dissolved in tetrahydrofuran (THF) over a palladium catalyst bed, catalyzing a polymerization reaction yielding regioregular poly(aryl ethynyl)-poly(aryl vinyl) (PPVE). A small sample of PPVE can be added to a NMR tube containing a solution of 99.9% deuterated chloroform ($CDCl_3$) and 0.1% tetramethylsilane (TMS). The dissolved PPVE can then be inserted into a proton (^1H) NMR spectrometer and undergo analysis to verify the purity and integrity of the resultant compound. The PPVE is expected to exhibit two aromatic peaks and one alkene peak in its NMR spectra.

[0036] One skilled in the art will appreciate that, for this and other processes and methods disclosed herein, the functions performed in the processes and methods may be implemented in differing order. Furthermore, the outlined steps and operations are only provided as examples, and some of the steps and operations may be optional, combined into fewer steps and operations, or expanded into additional steps and operations without detracting from the essence of the disclosed embodiments.

[0037] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[0038] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0039] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*e.g.*, bodies of the appended claims) are generally intended as "open" terms (*e.g.*, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases “at least one” and “one or more” to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles “a” or “an” limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases “one or more” or “at least one” and indefinite articles such as “a” or “an” (*e.g.*, “a” and/or “an” should be interpreted to mean “at least one” or “one or more”); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (*e.g.*, the bare recitation of “two recitations,” without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to “at least one of A, B, and C, etc.” is used, in general such a construction is intended in the sense of one having skill in the art would understand the convention (*e.g.*, “ a system having at least one of A, B, and C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to “at least one of A, B, or C, etc.” is used, in general, such a construction is intended in the sense of one having skill in the art would understand the convention (*e.g.*, “ a system having at least one of A, B, or C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0040] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0041] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art, all language such as "up to," "at least," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges, as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0042] From the foregoing, it will be appreciated that various embodiments of the present disclosure have been described herein for purposes of illustration, and that various modifications may be made without departing from the scope and spirit of the present disclosure. Accordingly, the various embodiments disclosed herein are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

CLAIMS

What Is Claimed Is:

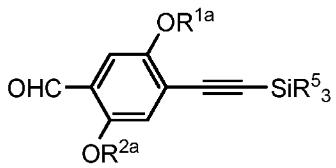
1. A method for making a polymer, the method comprising:

combining a silylalkynyl dialkoxyl arylaldehyde and a X-substituted dialkoxyl arylphosphonate; and

contacting the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate under conditions that provide for coupling of the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate to provide a X-substituted silylalkynyl diarylethene.

2. The method of claim 1, wherein coupling of the silylalkynyl dialkoxyl arylaldehyde and the X-substituted dialkoxyl arylphosphonate comprises Horner-Wadsworth-Emmons coupling.

3. The method of claim 1, wherein the silylalkynyl dialkoxyl arylaldehyde comprises a compound of Formula I:



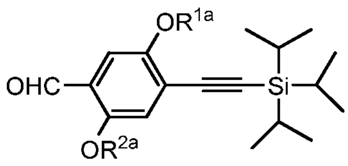
I

wherein:

each R^{1a} and R^{2a} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol; and

each R^5 is C_1-C_{20} alkyl.

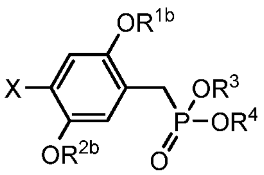
4. The method of claim 1, wherein the silylalkynyl dialkoxyl arylaldehyde comprises a compound of Formula Ia:



Ia

wherein each R^{1a} and R^{2a} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol.

5. The method of claim 1, wherein the X-substituted dialkoxyl arylphosphonate comprises a compound of Formula II:



II

wherein:

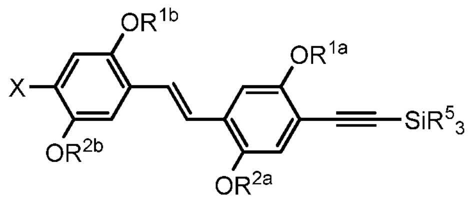
each R1b and R2b is, independently, C1-C20 alkyl, C2-C20 alkene, C2-C20 alkyne or alkylene glycol;

each R3 and R4 is, independently, C1-C20 alkyl; and

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate (CF3SO3-), mesylate (CH3SO3−), tosylate (CH3C6H4SO2-), or besylate (C6H5SO3-).

6. The method of claims 3, 4, and 5, wherein each R^{1a} and R^{1b} are the same and each R^{2a} and R^{2b} are the same.

7. The method of claim 1, wherein the X-substituted silylalkynyl diarylethene comprises a compound of Formula III:



III

wherein:

each R^{1a}, R^{1b}, R^{2a}, and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol;

R^5 is C_1-C_{20} alkyl; and

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate_($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).

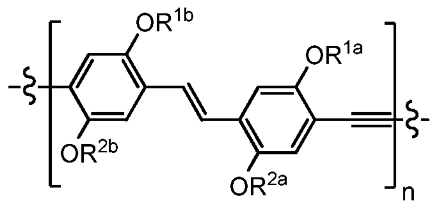
8. The method of claim 1, further comprising:

placing the X-substituted silylalkynyl diarylethene under conditions that allow the silyl moiety to be removed from the X-substituted silylalkynyl diarylethene to provide a X-substituted alkynyl diarylethene; and

placing the X-substituted alkynyl diarylethene under conditions that allow X-substituted alkynyl diarylethenes are coupled to provide the regioregular aryl ethynyl-aryl vinyl copolymer.

9. The method of claim 8, wherein coupling the X-substituted alkynyl diarylethene comprises a Sonogashira coupling.

10. The method of claim 8, wherein the regioregular aryl ethynyl-aryl vinyl copolymer comprises a compound of Formula IV:



IV

wherein:

each R^{1a}, R^{1b}, R^{2a}, and R^{2b}, independently, comprise C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol;

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate_($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$); and

n comprises an integer from 2 or more.

11. The method of claim 10, wherein n is an integer from 2 to 100.

12. The method of claim 10, wherein R^{1a} and R^{1b} are the same and R^{2a} and R^{2b} are the same.

13. The method of claim 1, further comprising contacting a silyl-alkynyl with a X-substituted dialkoxyl arylaldehyde under conditions that allow the silyl-alkynyl and X-substituted dialkoxyl arylaldehyde to react to provide the silylalkynyl dialkoxyl arylaldehyde.

14. The method of claim 13, wherein the silyl-alkynyl is selected from the group consisting of trimethylsilyl acetylene, *tert*-butyldimethylsilyl acetylene, tri-*iso*-propylsilyloxymethyl acetylene, and tri-iso-propylsilyl acetylene, or combinations thereof.

15. The method of claim 1, further comprising contacting a phosphonate containing compound and a X-substituted dialkoxyl arylaldehyde under conditions that allow the phosphonate containing compound and the X-substituted dialkoxyl arylaldehyde to react to provide the X-substituted dialkoxyl arylphosphonate monomer.

16. The method of claim 15, wherein contacting the phosphonate containing compound and the X-substituted dialkoxyl arylaldehyde comprises:

placing the X-substituted dialkoxyl arylaldehyde under conditions that allow the X-substituted dialkoxyl arylaldehyde to be reduced to provide a X-substituted dialkoxyl arylmethanol;

combining the X-substituted dialkoxyl arylmethanol with a leaving group containing compound under conditions that allow the leaving group containing compound to react with the X-substituted dialkoxyl arylmethanol to provide a X-substituted dialkoxyl arylmethyl-leaving group;

combining the X-substituted dialkoxyl arylmethyl-leaving group with a phosphite containing compound under conditions that allow the X-substituted dialkoxyl arylmethyl-leaving group with a phosphite containing compound to react; and

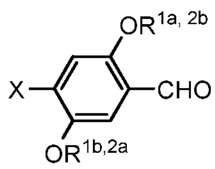
allowing an Arbuzov rearrangement to occur to provide the X-substituted dialkoxyl arylphosphonate monomer.

17. The method of claim 16, wherein the leaving group X comprises diazonium salt, oxonium ion, nonaflate, triflate, fluorosulfonate, tosylate, or mesylate .

18. The method of claim 16, wherein the leaving group X is mesylate.

19. The method of either of claim 13 or 15, further comprising contacting a C_1-C_6 alkoxy dihalide C_1-C_6 alkane with an unprotected X-substituted dialkoxyl arene under conditions that allow the C_1-C_6 alkoxy dihalide C_1-C_6 alkane and the unprotected X-substituted dialkoxyl arene to react to provide the X-substituted dialkoxyl arylaldehyde.

20. The method of claim 19, wherein the X-substituted dialkoxyl arylaldehyde comprises a compound of Formula V:



V

wherein:

each R^{1a}, R^{1b}, R^{2a}, and R^{2b}, independently, comprise C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol; and

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate_($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).

21. The method of claim 19, further comprising contacting a hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and an unprotected X-substituted monoalkoxyl *para*-substituted arene under conditions that allow the hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and the unprotected X-substituted monoalkoxyl *para*-substituted arene to react to provide the unprotected X-substituted dialkoxyl arene.

22. The method of claim 21, wherein the step of contacting comprises a Mitsunobu coupling.

23. The method of claim 22, wherein the Mitsunobu coupling is carried out using resin bound triphenylphosphine (PPh_3).

24. The method of claim 21, further comprising placing a protected X-substituted monoalkoxyl *para*-substituted arene under conditions that allow a protecting group to be

removed from the protected X-substituted monoalkoxyl *para*-substituted arene to provide the unprotected X-substituted monoalkoxyl *para*-substituted arene.

25. The method of claim 24, further comprising placing a protected monoalkoxyl arene under conditions that allow the protected monoalkoxyl arene to be halogenated to provide the protected X-substituted monoalkoxyl arene.

26. The method of claim 25, wherein the protected X-substituted monoalkoxyl arene comprises 3-halogen 4-(alkoxy)phenyl 1-protecting group.

27. The method of claim 25, further comprising contacting a protecting group containing compound and a monoalkoxyl *para*-substituted arene under conditions that allow the protecting group containing compound and the monoalkoxyl *para*-substituted arene to react to provide the protected monoalkoxyl *para*-substituted arene.

28. The method of claim 27, wherein the protecting group containing compound is selected from the group consisting of acetyl, benzoyl, benzyl, β-methoxyethoxymethyl ether, dimethoxytrityl, [bis-(4-methoxyphenyl)phenylmethyl], methoxymethyl ether, methoxytrityl [(4-methoxyphenyl)diphenylmethyl], *p*-methoxybenzyl ether, methylthiomethyl ether, pivaloyl, tetrahydropyranyl, trityl triphenylmethyl, silyl ether, trimethylsilyl ether, *tert*-butyldimethylsilyl ether, tri-*iso*-propylsilyloxymethyl ether, tri-*iso*-propylsilyl ether, ethoxyethyl ether, carbobenzyloxy, *p*-methoxybenzyl carbonyl, *tert*-butyloxycarbonyl, 9-fluorenylmethyloxycarbonyl, carbamate, *p*-methoxybenzyl, 3,4-dimethoxybenzyl, *p*-methoxyphenyl, tosyl, sulfonamide, and combinations thereof.

29. The method of claim 26, wherein the protecting group is a tosylate.

30. The method of claim 26, wherein the protected monoalkoxyl *para*-substituted arene is 4-(alkoxy)phenyl 4-protecting group.

31. The method of claim 26, wherein the protected monoalkoxyl *para*-substituted arene is 4-(alkoxy)phenyl 4-methylbenzensulfonate.

32. The method of claim 26, further comprising combining a *para*-substituted arene and a halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol under conditions that allow the *para*-substituted arene and the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol to provide a monoalkoxyl *para*-substituted arene.

33. The method of claim 32, wherein the *para*-substituted arene is hydroquinone.

34. The method of claim 32, wherein the monoalkoxyl *para*-substituted arene is 4-alkoxyphenol.

35. The method of claims 19 or 32, wherein hydroxylated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and the halogenated C_2-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol comprise different C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol moieties.

36. A method for producing a monomer, the method comprising:

providing a monoalkoxyl *para*-substituted arene;

placing the monoalkoxyl *para*-substituted arene under conditions that allow a protecting group to be introduced at a non-alkylenated substituent of the monoalkoxyl *para*-substituted arene to provide a protected monoalkoxyl *para*-substituted arene; and

placing the protected monoalkoxyl *para*-substituted arene under conditions that allow the protected monoalkoxyl *para*-substituted arene to be halogenated to provide a protected X-substituted monoalkoxyl arene.

37. The method of claim 36, further comprising:

placing the protected X-substituted monoalkoxyl arene under conditions that allow the protecting group to be removed from the protected X-substituted monoalkoxyl arene to provide an unprotected X-substituted monoalkoxyl arene; and

placing the an unprotected X-substituted monoalkoxyl arene under conditions that allow an aldehyde to be introduced onto the unprotected X-substituted monoalkoxyl arene to provide a X-substituted arylaldehyde.

38. The method of claim 37, further comprising combining a hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and an unprotected X-substituted monoalkoxyl arene under conditions that allow the hydroxylated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol and the unprotected X-substituted monoalkoxyl arene to react to provide the unprotected X-substituted dialkoxyl arene.

39. The method of claim 38, wherein reacting comprises a Mitsunobu coupling.

40. The method of claim 39, wherein the Mitsunobu coupling is carried out using resin bound triphenylphosphine (PPh_3).

41. The method of claim 37, further comprising placing the X-substituted arylaldehyde under conditions that allow a silylalkynyl to be introduced onto the X-substituted arylaldehyde to provide a silylalkynyl arylaldehyde.

42. The method of claim 41, wherein the silylalkyneyl is selected from the group consisting of trimethylsilyl acetylene, *tert*-butyldimethylsilyl acetylene, tri-*iso*-propylsilyloxymethyl acetylene, tri-*iso*-propylsilyl acetylene, and combinations thereof.

43. The method of claim 37, further comprising placing the X-substituted arylaldehyde conditions that allow a phosphonate to be introduced onto the X-substituted arylaldehyde to provide a X-substituted arylphosphonate.

44. The method of claim 43, wherein placing the X-substituted arylaldehyde conditions that allow a phosphonate to be introduced comprises:

placing the X-substituted arylaldehyde under conditions that allow the X-substituted arylaldehyde to be reduced to provide a X-substituted arylmethanol;

placing the X-substituted arylmethanol under conditions that allow a leaving group to be introduced onto the X-substituted arylmethanol to provide a X-substituted arylmethyl-leaving group;

placing the X-substituted arylmethyl-leaving group under conditions that allow the leaving group to be substituted of the X-substituted arylmethyl-leaving group with a phosphite; and

allowing an Arbuzov rearrangement to occur to provide a X-substituted arylphosphonate.

45. The method of claim 44, wherein the leaving group X is selected from the group consisting of diazonium salt, oxonium ion, nonaflate, triflate, fluorosulfonate, tosylate, mesylate, and combinations thereof.

46. The method of claim 44, wherein the leaving group is mesylate.

47. The method of claims 41 to 43, further comprising combining the silylalkynyl arylaldehyde and the X-substituted arylphosphonate under conditions that allow the silylalkynyl arylaldehyde and the X-substituted arylphosphonate to react to create a X-substituted silylalkynyl diarylethene.

48. The method of claim 47, wherein reacting comprises a Horner-Wadsworth-Emmons coupling.

49. The method of claim 47, further comprising:

placing the X-substituted silylalkynyl diarylethene under conditions that allow the silyl to be removed to provide X-substituted alkynyl diarylethene; and

contacting the X-substituted diarylethene alkynyl diarylethene under conditions that allow the X-substituted diarylethene alkynyl diarylethene to be coupled to provide a regioregular poly(aryl ethynyl)-poly(aryl vinyl).

50. The method of claim 49, wherein coupling comprises a Sonogashira coupling.

51. The method of claim 36, further comprising:

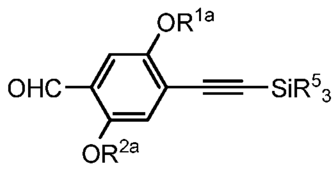
providing a *para*-substituted arene and a halogenated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; and

contacting the *para*-substituted arene and the halogenated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol under conditions that allow the *para*-substituted arene and the halogenated C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol to react to provide a monoalkoxyl *para*-substituted arene.

52. The method of claim 51, wherein the *para*-substituted arene comprises hydroquinone.

53. The method of claim 51, wherein the monoalkoxyl *para*-substituted arene comprises 4-alkoxyphenol.

54. A compound of general of Formula I:



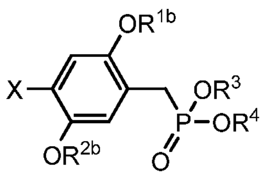
I

wherein:

each R^{1a} and R^{2a} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol; and

each R^5 is, independently, C_1-C_{20} alkyl.

55. A compound of general Formula:



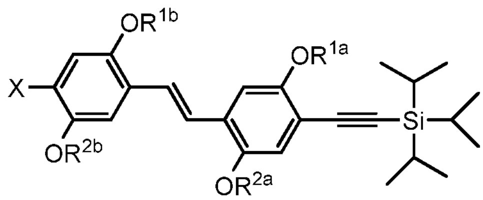
wherein:

each R^{1b} and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne or alkylene glycol;

each R^3 and R^4 is, independently, C_1-C_{20} alkyl; and

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate_($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).

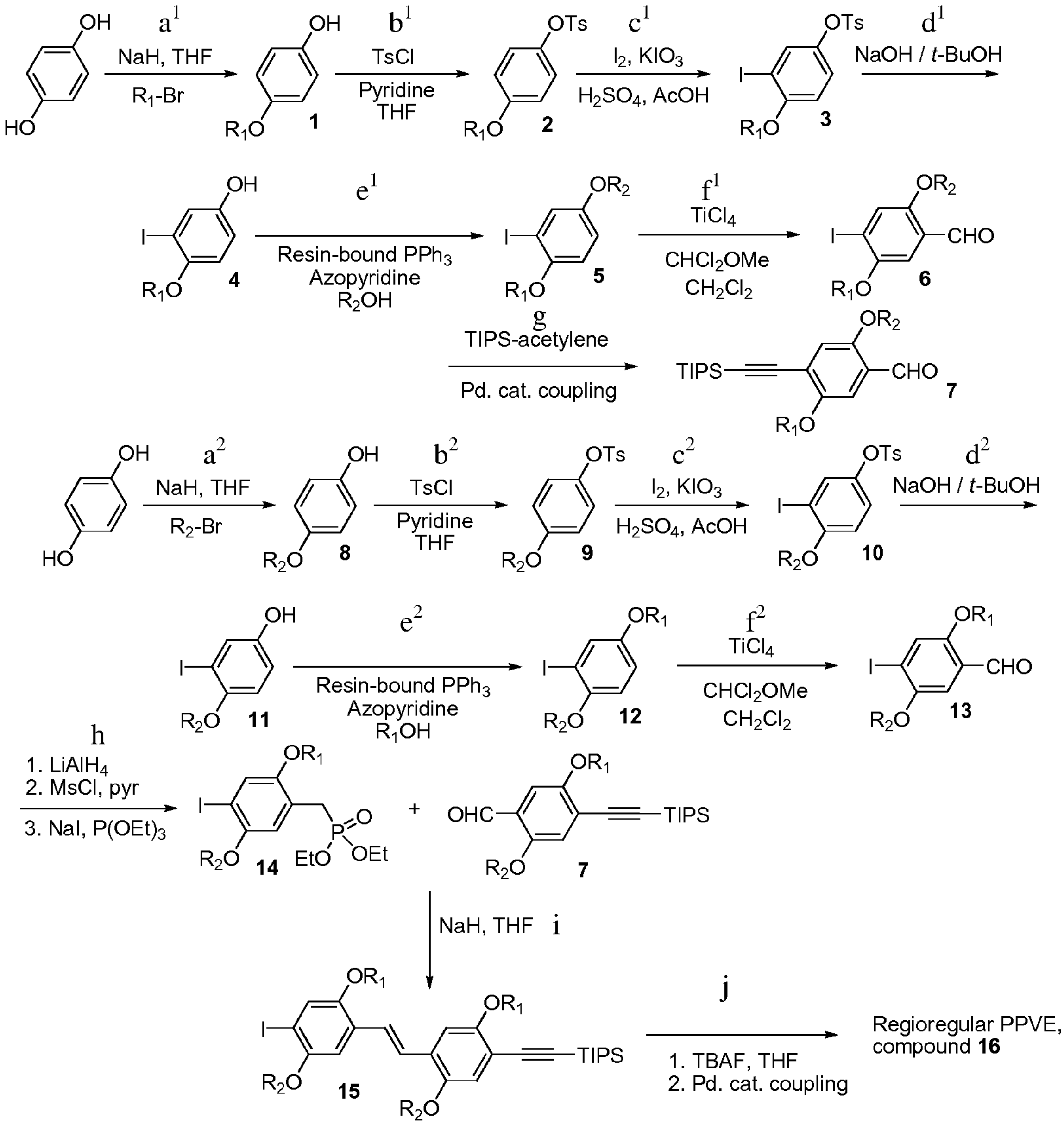
56. A compound of general Formula:



wherein:

each R^{1a}, R^{1b}, R^{2a}, and R^{2b} is, independently, C_1-C_{20} alkyl, C_2-C_{20} alkene, C_2-C_{20} alkyne, or alkylene glycol; and

X is hydroxide, alkoxide, astatine, iodine, bromine, chlorine, or fluorine, triflate_($CF_3SO_3^-$), mesylate ($CH_3SO_3^-$), tosylate ($CH_3C_6H_4SO_2^-$), or besylate ($C_6H_5SO_3^-$).


a1
NaH, THF
R1-Br
b1
TsCl
Pyridine
THF
c1
I2, KIO3
H2SO4, AcOH
d1
NaOH / t-BuOH
e1
Resin-bound PPh3
Azopyridine
R2OH
f1
TiCl4
CHCl2OMe
CH2Cl2
g
TIPS-acetylene
Pd. cat. coupling
a2
NaH, THF
R2-Br
b2
TsCl
Pyridine
THF
c2
I2, KIO3
H2SO4, AcOH
d2
NaOH / t-BuOH
e2
Resin-bound PPh3
Azopyridine
R1OH
f2
TiCl4
CHCl2OMe
CH2Cl2
h
1. LiAlH4
2. MsCl, pyr
3. NaI, P(OEt)3
NaH, THF i
j
1. TBAF, THF
2. Pd. cat. coupling
Regioregular PPVE, compound 16
1
2
3
4
5
6
7
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11
12
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14
15

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/54147

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08G 61/12 (2012.01)
USPC - 526/72
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) -C08G 61/12 (2012.01)
USPC -526/72

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, WIPO, Google Patent, Google Scholar, SureChem (phosphonate, aryl, benzyl, aldehyde, methoxy, polymer, dialkoxy, formula, horner, wadsworth, silyl, halogenated, emmons, para, protected, phenol, luminescent, monomer, coupling, aryl, mitsunobu, phosphoryl,brizius, trimethylsilyl, electron, arene, ots)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y --- A	US 5,653,914 A (HOLMES, et al.) 05 August 1997 (05.08.1997) entire document, especially col 6, ln 46-55; col 9, ln 5-10, 40-52	55 --- 1-5, 7-34
Y	US 2008/0249280 A1 (KAGEYAMA, et al.) 09 October 2008 (09.10.2008) entire document, especially para[0104], [0213], [0248]	55
Y	Wang, Hsian-Wen, et al. "Coupling of FRET and Photoinduced Electron Transfer in Regioregular Silylene-Spaced Energy Donor-Acceptor-Electron Donor Copolymers." Macromolecules 41.8 (25 March 2008): 2762-2770	56
Y	US 2010/0283006 A1 (AJAYAGHOSH, et al.) 11 November 2010 (11.11.2010) entire document, especially para[0019]	56
A	US 2002/0193532 A1 (IKEHIRA, et al.) 19 December 2002 (19.12.2002) entire document, especially para[0106]	1-5, 7-34
A	US 2007/0197768 A1 (CHOI, et al.) 23 August 2007 (23.08.2007) entire document, especially para[0077]	1-5, 7-34
A	WO 2009/015897 A1 (LEONARDI, et al.) 05 February 2009 (05.02.2009) entire document, especially pg 35, ln 8-14	1-5, 7-34

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

* 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 another 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	Date of mailing of the international search report
02 November 2012 (02.11.2012)	20 NOV 2012

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:
Lee W. Young
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/54147

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6, 35
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/54147

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,360,686 A (WANG, et al.) 23 November 1982 (23.11.1982) entire document, especially col 4, Table 1	36-53
A	US 5,290,939 A (SEDELMEIER, et al.) 01 March 1994 (01.03.1994) entire document, especially col 5, ln 52 to col 6, ln 9	36-53
A	US 4,587,315 A (LAU) 06 May 1986 (06.05.1986) entire document, especially col 3, ln 1-8; col 4, ln 35-50	54
A	US 2005/0176915 A1 (CHO, et al.) 11 August 2005 (11.08.2005) entire document, especially para[0002]; pg 36	54