Articles

Synthetic Approaches to Regioregular Unsymmetrical Dialkoxy-Substituted Poly(1,4-phenylene ethynylene)s

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ABSTRACT: Poly(2,5-disubstituted-1,4-phenylene ethynylene)s, PPEs, are generally synthesized by Pd-catalyzed coupling polymerizations of appropriately substituted 1,4-diiodobenzenes and 1,4-diethynylbenzenes (i.e., condensation polymerization of A−A and B−B type monomers). If the monomers are not symmetrically substituted, this results in an irregular substitution pattern of the side chains along the polymer backbone. As with other classes of conjugated polymers, the relative placement of side chains along the backbone should influence the properties of the materials. We report a new synthetic approach to prepare regioregular unsymmetrically substituted PPEs by polymerization of 4-iodophenylacetylenes (i.e., a condensation polymerization of a single A−B type monomer). We have synthesized both the regiorandom and regioregular PPEs from unsymmetrically substituted monomers. We provide a detailed discussion of various approaches to the synthesis of PPEs with different regioregularities and provide a preliminary description of the differences between regioregular and regiorandom analogues.

Introduction

Conjugated polymers exhibit interesting electronic and optical properties and have great commercial potential as semiconductors for use in light-emitting diodes, field effect transistors, solar cells, and sensors.[1] While the charge carrier mobility of conjugated polymers is typically lower than that of doped silicon, the ease of processing (i.e., from solution or the melt) and the ability to tailor material properties through modification of the molecular structure provide opportunities for use of these materials in power efficient, flexible, robust, and inexpensive consumer devices.

It is well established that the identity and relative position of side chains along the polymer backbone have a large impact on the properties of poly(alkylthiophene)s. Jen et al. initially incorporated flexible alkyl side chains onto the backbone of polythiophene to develop soluble conjugated organic materials.[2] Defining the two 2- and 5-positions of a 3-alkylthiophen-2,5-diyl repeat unit of the polymer as the "head" (*h*) and "tail" (*t*), respectively, gives rise to three possible regiochemically distinct diads: *hh*, *ht*, and *tt*. Oxidative polymerization of 3-alkylthiophenes affords materials with a mixture of these three diads along the backbone (Figure 1A). McCullough et al. and Reike et al. later independently realized the importance of controlling the relative position of the side chains of poly(3-alkylthiophene) through development of new synthetic methods.[3,4] Polymerization of 5-metallo-2-bromo-3-alkylthiophenes by organometallic coupling affords a regioregular polymer primarily consisting of *ht* diads (Figure 1B). Regioregularity has a large impact on the properties of poly(3-alkylthiophene)s: The regioregular materials possess higher crystallinity, red-shifted optical absorptions, greater conductivity, and a smaller band gap than the regiorandom analogues.[5] However, the effect of the relative position of substituents on the properties of other classes of conjugated polymers has been restricted to poly(3-alkylthienylene vinylene),[6] poly[3-alkyl-2,5-thienylene-1,4-phenylene],[7] poly(1,4-phenylenevinylene)s,[8] and poly(biphenylenevinylene).[9]

Poly(1,4-phenylene ethynylene)s, PPE, are a particularly interesting class of conjugated polymers due to their attractive electronic and optical properties.[10] They have been used as semiconductors and/or fluorescent materials in field effect transistors,[11] light-emitting diodes,[12] solar cells,[13] and sensors.[14] Symmetrically 2,5-disubstituted PPEs (i.e., X = Y in Figure 1C) are inherently regioregular. While there are numerous examples of PPEs prepared from monomers bearing pairs of dissimilar side chains on the phenylene rings,[15−18] the polymerization of unsymmetrically substituted 1,4-diethynylbenzenes and 1,4-diiodobenzenes by alkyne−aryl iodide[10] coupling (i.e., by an A−A + B−B type condensation polymerization), or by alkyne metathesis of diethynes,[19] yields regiorandom PPEs containing a mixture of *hh*, *tt*, and *ht* diads (Figure 1C). The effect of regioregularity of PPEs has not been explored extensively.[20] We have recently developed synthetic routes to allow for the preparation of regular (*ht*) unsymmetrically substituted PPEs by polymerization of 2,5-disubstituted-4-iodophenylacetylenes, i.e., difunctional A−B type monomers bearing dissimilar alkoxy side chains (Figure 2) (previous reports on preparation of PPEs by polymerization of A−B type monomers have been restricted to those with identical side chains to give symmetrical, inherently regioregular analogues[21−23]). Following a preliminary communication,[24] we now provide a detailed exploration of synthetic approaches to regioregular and regiorandom PPE analogues, present optimized synthetic procedures, demonstrate control over regioregularity (using ^{1}H and ^{13}C NMR spectroscopy), and report on the effect of regioregularity on the supermolecular packing (X-ray dif-

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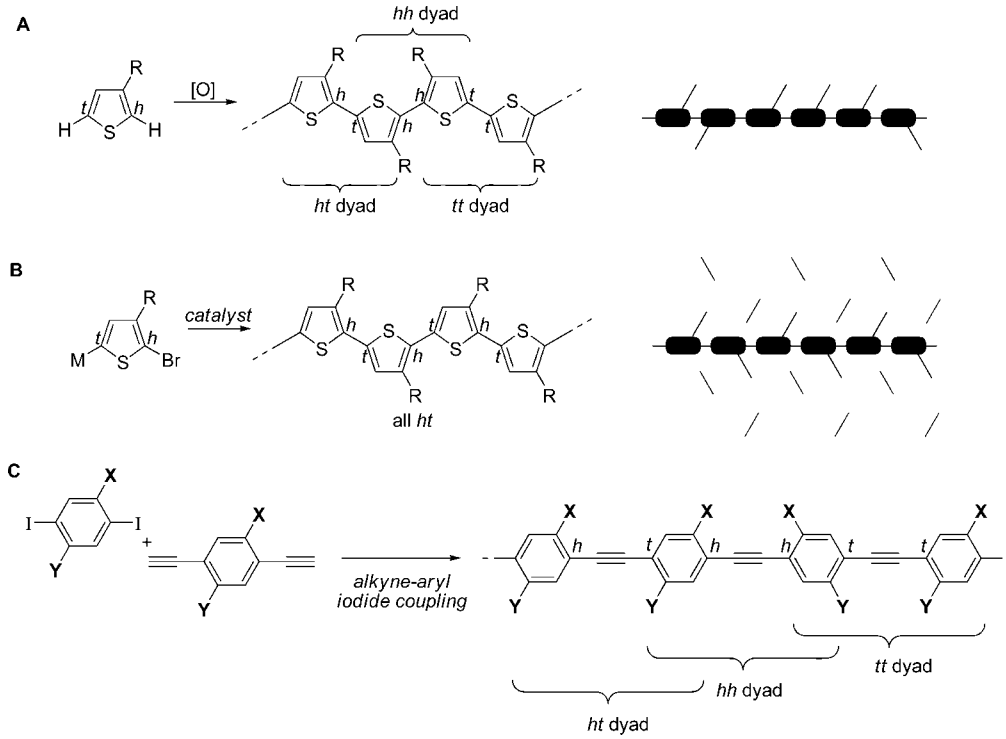


Figure 1. (A) Oxidative polymerization of 3-alkylthiophenes affords regiorandom materials consisting of *ht*, *hh*, and *tt* diads. (B) Regioselective polymerization affords regioregular *ht* polymers which crystallize as a result of side-chain packing. (C) Polymerization of unsymmetrically substituted 1,4-diodobenzenes and 1,4-diethynylbenzenes affords a regiorandom PPE.

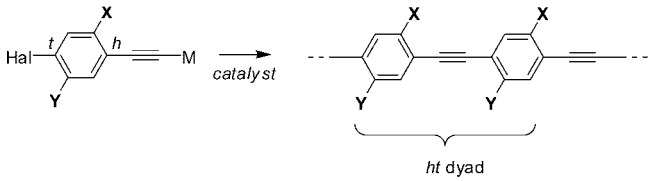
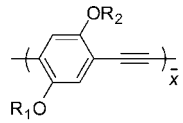


Figure 2. Preparation of regioregular unsymmetrically substituted PPEs from an A−B type monomer.



	regiorandom	regioregular
R_1 = *n*-$C_{12}H_{25}$; R_2 = CH_3	**RnPPE(12/1)**	**RgPPE(12/1)**
R_1 = *n*-$C_{12}H_{25}$; R_2 = *n*-C_6H_{13}	**RnPPE(12/6)**	**RgPPE(12/6)**
R_1 = R_2 = *n*-$C_{12}H_{25}$		**PPE(12)**

Figure 3. Regioregular (Rg) and regiorandom (Rn) poly(phenylene ethynylyne)s, **PPE(*m*/*n*)**, examined in this study.

fraction) and electronic structure (UV−vis spectroscopy) of the materials. While this report is restricted to the development of methodology using combinations of dissimilar linear alkoxy side chains, we expect that these approaches will provide for greater control over the assembly and properties of amphiphilic analogues and those bearing functional side chains.

Results and Discussion

To fully explore the synthesis of regioregular unsymmetrically substituted PPEs, we prepared and characterized both regioregular (Rg) and regiorandom (Rn) analogues of poly(2,5-dialkoxy-1,4-phenylene ethynylene)s bearing dodecyloxy, hexyloxy, and methoxy side chains (Figure 3). A symmetrically substituted analogue with two dodecyloxy side chains was prepared for comparison. Regiorandom polymers were prepared by polymerization of suitably substituted diiodoarenes and diethynylarenes (i.e., combination of two difunctional monomers A−A and B−B) (Figure 1C). The regioregular analogues were synthesized by polymerization of a single 2,5-disubstituted 4-iodophenylene acetylene (i.e., a single A−B type monomer) (Figure 2).

Synthesis of Regiorandom PPEs from A−A and B−B Type Monomers. Regiorandom PPEs were prepared by the palladium-catalyzed cross-coupling condensation of 2,5-dialkoxy-1,4-diiodobenzenes **1** and 2,5-dialkoxy-1,4-diethynylbenzenes **2** (Figure 4). The monomers were prepared using well-precedented procedures whereby 1,4-dialkoxybenzenes were subjected to diiodination (I_2, KIO_3, H_2SO_4, AcOH) to afford **1**, followed by ethynylation (TMS−acetylene, $Pd(PPh_3)_4$, CuI, followed by *n*-Bu_4NF) to give **2** (see Supporting Information).

Synthesis of Regioregular PPEs by Polymerization of A−B Type Monomers. The preparation of the regioregular *ht* unsymmetrically substituted alkoxy PPEs relies on the synthesis of A−B type monomer **11** bearing both the iodo and ethynyl substituents (Figure 5). The substitution pattern of the A−B monomer sets the relative placement of the substituents in the resulting polymer. There is a challenge of installing the iodo and ethynyl substituents in specific positions adjacent to two dissimilar alkoxy substituents. This was achieved by tosylation of 4-alkoxyphenol (**3**) (TsCl, pyridine) to provide **4** in which the tosyl group lowers the electron-donating ability of the oxygen. This assures that subsequent iodination takes place ortho to the alkoxy group, resulting in the monoiodinated tosylate **5**.[25] The tosylate group was then removed by base-promoted hydrolysis to afford the monoiodinated phenol **6**. Alkylation of the 4-alkoxy-3-iodophenol using a Mitsunobu reaction (*n*-alcohol, DEAD, Ph_3P) or by Williamson ether synthesis (NaH, alkyl bromide) provided the 1,4-dialkoxy-2-iodobenzenes **7** (Figure 5).

Our initial synthesis of the 4-iodophenylacetylene monomer **11a** made use of Friedel−Crafts acetylation followed by

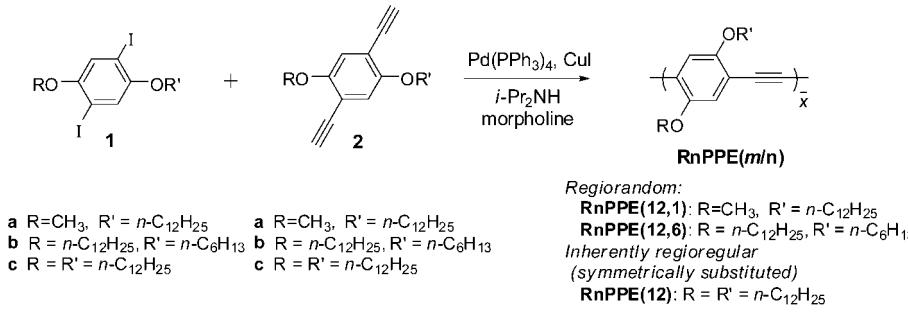


Figure 4. Preparation of regiorandom polymers **RnPPE(*m*/*n*)** by polymerization of diiodobenzene (**1**) and diethynylbenzene (**2**).

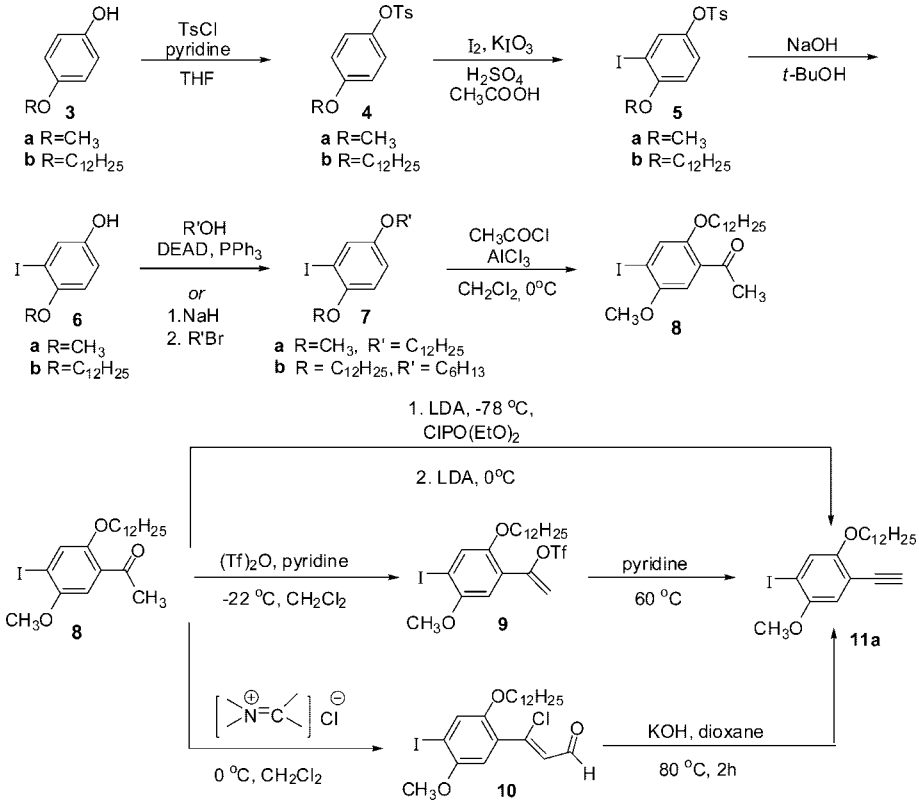


Figure 5. Synthesis of A−B monomer for the preparation of regioregular dodecyloxy/methoxy polymer, **RgPPE(12/1)**.

dehydration of the resulting acetophenone. Friedel−Crafts acylation[26] (AcCl, $AlCl_3$) affords the acetophenone derivative **8** in good yield, with the desired substitution pattern arising from the ortho/para electronic directing effects and steric bulk of the iodine (Figure 5). We attempted several methods to efficiently convert the methyl ketone of **8** into an ethynyl group. We initially used Stang's base-promoted elimination for an enol triflate[27] whereby the acetyl group is converted to an enol triflate and subsequent elimination is promoted by pyridine. Treatment of the acetophenone **8** with triflic anhydride in the presence of pyridine at −22 °C gives triflate **9**, which on heating with excess pyridine at 60 °C undergoes elimination to give the alkyne **11a** (Figure 5). However, preparation of the vinyl triflate proceeded with low conversion (25−40%). The in situ conversion of the triflate to the alkyne resulted in the formation of number of side products which were inseparable by column chromatography. Attempts to isolate the triflate were thwarted by rapid hydrolysis. In a related approach to prepare the alkyne, we attempted the Vilsmeier haloformylation[28] of the acetyl group followed by a KOH-promoted Bodendorf reaction.[29] Reaction of benzophenone **8** with excess Vilsmeier complex at 0 °C formed a mixture of *E* and *Z* β-chloroaldehydes **10** (Figure 5) with high conversion (90%). The mixture of β-chloroaldehydes was treated in situ with KOH, resulting in complete conversion to the alkyne. However, analysis of the product (after separation by column chromatography) by ^{1}H NMR spectroscopy and mass spectrometry revealed the presence of a considerable amount (as much as 25%) of the analogous 4-chlorophenylacetylene in which the iodo substituent is replaced by chlorine. The two compounds appeared as a coincident spot by TLC, and it was not possible to separate the components by column chromatography. While we could lower the amount of the chlorine substituted impurity by using only a stoichiometric amount of Vilsmeier complex, we were unable to completely suppress the formation of the chlorinated byproduct. Monomer **11a** was successfully prepared from acetophenone **8** by the Negishi−Tour phosphonation−elimination procedure. Treatment of **8** with LDA and $ClPO(OEt)_2$ followed by base-promoted elimination with LDA[30] afforded the desired monomer **11a** (Figure 5). While the Negishi−Tour phosphonation−elimination route worked well for analogues with hydrocarbon side chains, use of a strong base (LDA) represents a serious limitation to this method. This led us to also explore formylation of **7b** followed by homologation to synthesize the 2,5-dialkoxy-4-iodophenylacetylene monomer **11b** (Figure 6). Formylation of monoiodobenzene **7b** ($TiCl_4$, $CHCl_2OCH_3$) at low temperature (−15 to −40 °C)

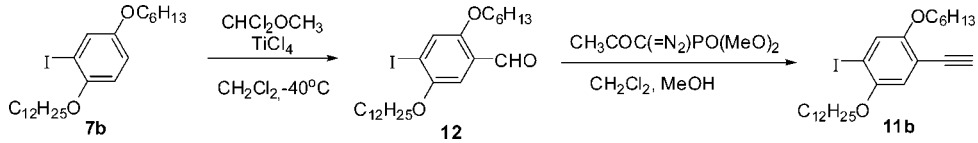


Figure 6. Synthetic scheme for preparing monomer **13b** using formylation−homologation.

provided benzaldehyde **12**. Analysis of the crude reaction mixture indicated the formation of a 2,5-dialkoxy-4-iodobenzaldehyde as the major product, but several byproducts are also formed. The crude reaction mixture gave a ^{1}H NMR spectrum that included the presence of three different aldehydes (see Supporting Information). Analysis of the aromatic region of the spectrum allowed for identification of these side products. The desired product gives singlets at 7.45 and 7.18 ppm. The remaining signals in the aromatic region of the spectrum indicate the presence of a trisubstituted benzene: δ 7.30 (d, $^4J_{HH} = 3$ Hz), δ 7.11 (dd, $^4J_{HH} = 3.3$ Hz, $^3J_{HH} = 9$ Hz), and δ 6.91 (d, $^3J_{HH} = 9$ Hz). These protons are further downfield than the starting material and are consistent with literature values for a 2,5-dialkoxybenzaldehyde, which is formed by electrophilic aromatic substitution of the iodo substituent for a formyl group. The presence of a regioisomer of the desired product was shown by mass spectrometry and can be identified from the appearance of a singlet at 6.93 ppm in the ^{1}H NMR spectrum as a 2,5-dialkoxy-3-iodobenzaldehyde (i.e., from formylation meta to the iodo substituent). The 3,6-dialkoxy-2-iodobenzaldehyde regioisomer (formed by formylation ortho to the iodo substituent) is not formed, likely due to steric interactions with the iodine. Two other byproducts formed during this reaction are 1,4-dialkoxybenzene and 1,4-dialkoxy-2,5-diiodobenzene. The signals for the aromatic protons of these compounds occur at 6.8 and 7.18 ppm, respectively. The former arises from protonation of the starting material followed by electrophilic loss of iodine to a second molecule of starting material to give the di-iodinated material. Column chromatography allowed for separation of each of these byproducts and mass spectroscopy was used to verify the molecular weights of the side products. The overall conversion to the desired product is 61%, and the remaining 39% is accounted for in the byproducts: 1,4-dialkoxy-2,5-diiodobenzene (6%), 1,4-dialkoxybenzene (3%), 2,5-dialkoxybenzaldehyde (18%), and 2,5-dialkoxy-3-iodobenzaldehyde (12%).

The desired product was purified by column chromatography followed by recrystallization. The formyl group was converted to the ethynyl substituent using the Seyferth−Gilbert procedure.[31] Treatment of the benzaldehyde **12** with $CH(=N_2)PO(OCH_3)_2$ and potassium *tert*-butoxide resulted in the formation of phenylacetylene **11b**. The use of a strong base (*t*-BuOK) and relatively expensive Seyferth reagent led us to explore the use of milder and cheaper Bestman−Ohiro homologation procedure whereby aldehyde **12** was treated with $CH_3COC(=N_2)CPO(OCH_3)_2$ and K_2CO_3 in $MeOH/CH_2Cl_2$ to give alkyne **11b** in high yield (Figure 6).

The 4-iodophenylacetylene monomers (**11**) were polymerized using a Pd-catalyzed condensation polymerization. Palladium tetrakis(triphenylphosphine) and CuI were used as the catalyst and cocatalyst, respectively. A combination of morpholine, diisopropylamine, and toluene kept the polymer soluble throughout the course of the reaction. We observed fluorescence immediately upon heating the polymerization mixture to 70 °C. The reaction was continued for 3−4 days to ensure complete conversion, and the polymer was precipitated and then fractionated by extraction with different solvents.

Polymer Structure. The molecular structures of the polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy and gel permeation chromatography.

Table 1. Molecular Weights of PPEs

	$M_n/10^3$ g mol^{-1}	
	^{1}H NMR end-group analysis	GPC[a]
RnPPE(12/1)	8.7	18
RgPPE(12/1)	8.2	12
RnPPE(12/6)	17	38
RgPPE(12/6)	6.2	15

[a] Calibrated with polystyrene standards.

Molecular weights of the polymers were determined by GPC and end-group analysis by ^{1}H NMR spectroscopy. The PPE polymer chains have iodophenyl or phenylacetylene end groups. The chemical shift of the aromatic proton ortho to the iodide is further downfield (δ 7.3 ppm) than the protons on the polymer backbone ($\sim\delta$ 7.1 ppm). In contrast, the aromatic proton ortho to the alkyne end group is easily distinguished, occurring at around δ 6.9 ppm. The signals of the other proton associated with each of these end groups are coincident with signals for protons in the polymer backbone. In a traditional polymerization of diiodo and diethynyl monomers, a slight stoichiometric imbalance leads to different amounts of the iodo and ethynyl end groups. In this case the average amount of the two end groups was considered when calculating the number of repeat units present in the polymer. However, synthesis of regioregular polymers from A−B type 4-iodophenylacetylene monomers leads to chains bearing one end group of each type, as confirmed by the equal integrals for the peaks at δ 6.9 and δ 7.3 ppm for polymers prepared in this manner. The molecular weights of the polymers obtained by ^{1}H NMR and GPC are shown in Table 1. The molecular weights obtained by GPC are consistently higher than those determined by end-group analysis, which can be explained by the relatively large hydrodynamic volume of the rigid-rod PPE compared to the coiled conformation of the polystyrenes used as a standard for GPC measurements.[10]

The regioregularity of the polymers was determined by examining the regions of the ^{1}H and ^{13}C NMR spectra corresponding to the nuclei of the 1,4-phenylene units (as well as the methyl signals for analogues of **PPE(12/1)**). These nuclei give signals at different chemical shifts depending on the environment imposed by the relative placement of substituents along the polymer. The effect of regioregularity is most obvious in the difference between the spectra of regiorandom and regioregular **PPE(12/1)**. These differences can be understood in terms of the presence of the three diads expected in the polymer structures (Figure 7).

The **RgPPE(12/1)** polymer gives rise to a single sharp resonance in the aromatic region which can be assigned to the aromatic proton in the *ht* (*th*) linkage (Figure 8A (bottom)). The proton in the 3-position (ortho to dodecyloxy substituent) and in the 6-position (ortho to the methoxy substituent) have a coincident chemical shift. This is in contrast to the regiorandom analogue, **RnPPE(12/1)**, which displays three singlets in the aromatic region of the ^{1}H NMR spectrum (Figure 8A (top)). These arise from the presence of three diads *hh*, *tt*, and *ht* (*th*) (Figure 7).

The differences in the chemical shifts of the protons in each diad can be understood in terms of the steric crowding experienced by the relevant hydrogen atom. Greater steric crowding around a hydrogen atom results in downfield shift arising from a perturbation of the electron distribution around

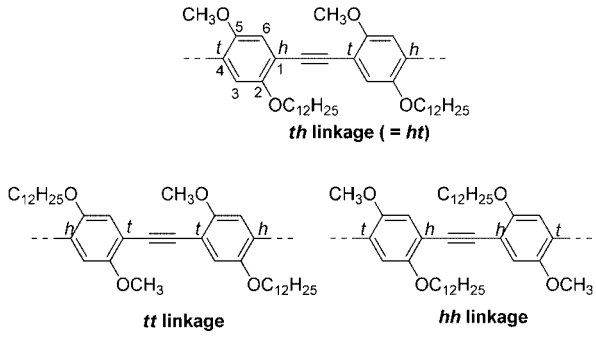


Figure 7. Three possible diads in the regiorandom **PPE(12/1)** polymer.

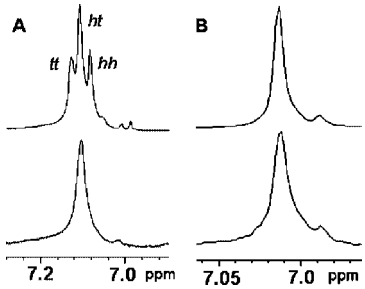


Figure 8. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) spectra. (A) **PPE(12/1)**: top, regiorandom; bottom, regioregular. (B) **PPE(12/6)**: top, regiorandom; bottom, regioregular.

the nucleus. The aromatic protons in the 3-position of the phenylene ring of the *tt* linkage, i.e., between the smaller methoxy side chains, experience the least steric hindrance and give rise to a singlet with a lower chemical shift (δ 7.0 ppm). Likewise, the proton in the 5-position in the *hh* linkage experiences the highest steric crowding due to the two dodecyloxy groups and is shifted further downfield (δ 7.04 ppm). The protons in 3- and 5-positions in the *ht* (*th*) diads (between the dodecyloxy and methoxy side chain) are represented by the central peak, which appears at the same chemical shift as the singlet for the aromatic protons of the regioregular (*ht*) regioregular analogue **RgPPE(12/1)**. The ratio of peak intensities (1:2:1) in this region of the spectrum of the regiorandom material reflects what would be expected on the basis of a statistical distribution of diads.

The signals for the aromatic protons for both the **RnPPE(12,6)** (Figure 8B, top) and **RgPPE(12,6)** (Figure 8B, bottom) polymer appear as a sharp singlet at 7.01 ppm. This is in contrast to the ^{1}H NMR spectra of **PPE(12/1)**, in which the complexity of the peaks in the regiorandom material can be ascribed to the different environments generated by relative placement of the dodecyl and methyl groups (see above). For the **PPE(12/6)** polymers, although the alkoxy side chains are different, they are both long enough to impart a similar steric environment around the respective nuclei of the backbone for all the three types of diads.

The ^{13}C NMR spectra of the polymers also provide evidence for the different relative placement of substituents in regioregular and regiorandom polymers. For the regiorandom polymer **RnPPE(12/1)**, the peaks for C2 and C5 (i.e., carbon atoms bearing the alkoxy groups) appear as four closely spaced peaks at around 154.0 ppm and two peaks at approximately 154.4 ppm (Figure 9A (top)). This can be ascribed to the presence of the different linkages present in the regiorandom material, with separate signals for C2 in an *ht* and *hh* diad, and for C5 in *th* and *tt* diads (the chemical shift of C2 in the *tt* diad and C5 of the *hh* diad, shown in Figure 7, is influenced primarily by the relative placement of substituents in the next repeat unit, i.e., the next diad). In contrast, the signals for these carbons in the **RgPPE(12/1)** regioregular polymer (Figure 9A (bottom)) containing only *ht* diads appear as single sharp peaks at 154.0 ppm for C2 and at 154.4 ppm for C5. The signals for C3 and C6 (the unsubstituted positions) appear as a single peak at 116.9 ppm in the regioregular sample, whereas in the spectrum for the regiorandom material these carbons appear as two closely spaced peaks (116.8 and 117.1 ppm). Likewise, the ^{13}C peak of the methoxy substituent of the regioregular **RgPPE(12/1)** gives a sharp signal at 70.4 ppm while there are two peaks (70.3 and 70.5 ppm) for the regiorandom sample. The C1 and C4 carbons of the phenylene appear as a single peak for both **RnPPE(12/1)** and **RgPPE(12/1)**. These carbons lie in the backbone of the polymer, and the chemical shift is apparently not influenced by the differences in the steric environment arising from substituents on the neighboring ring.

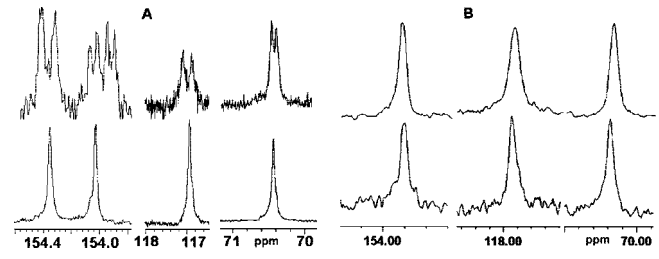


Figure 9. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) spectra of the aromatic regions. (A) **PPE(12/1)**: top, **RnPPE(12/1)**; bottom, **RgPPE(12/1)**. (B) **PPE(12/6):** top, **RnPPE(12/6)**; bottom, **RgPPE(12/6)**.

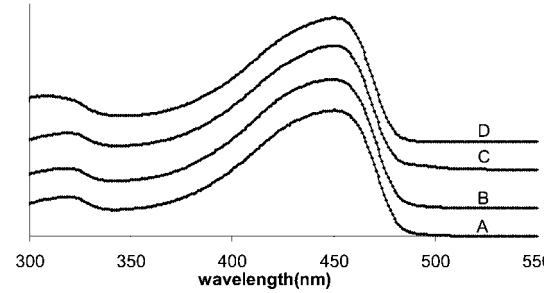


Figure 10. UV−vis spectra of polymer solutions ($CHCl_3$): (A) **RnPPE(12/1)**, (B) **RgPPE(12/1)**, (C) **RnPPE(12/6)**, and (D) **RgPPE(12/6)**.

The C2 and C5 carbons (bearing the alkoxy groups), C3 and C6 carbons (bearing the aromatic protons), and carbons of the methylene units of the side chains attached to the oxygen for the **PPE(12/6)** polymers are shown in Figure 9B (left to right, respectively). All the peaks are sharp and the spectra of regioregular and regiorandom polymers are indistinguishable.

Electronic Structure. The optical absorptions of conjugated polymers can be correlated to the degree of conjugation along the backbone and can therefore be related to the molecular structure. The twisting around the backbone arising from the steric interactions between side chains on adjacent repeat units, and the supermolecular packing, may both have a strong influence on the electronic spectra. The spectra of the polymers were investigated in solution and the solid state. The absorption spectra obtained for the polymers in $CHCl_3$ solution are shown in Figure 10. Regiorandom and regioregular analogues of the **PPE(12/1)** and **PPE(12/6)** polymers have essentially identical spectra in solution. The absorption spectra exhibit a weak absorption band at around 320 nm and a broad main transition centered around 451 nm. These spectra are similar to symmetrically substituted PPEs in solution and are consistent with the low rotational barrier of the PPE subunits (estimated to be <1 kcal mol^{-1}).[10]

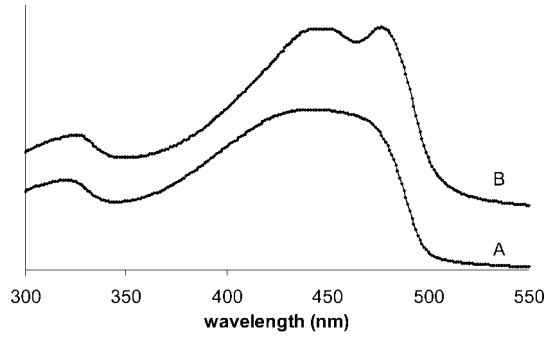


Figure 11. UV−vis spectra of polymer films: (A) **Rn(12/1)**; (B) **Rg(12/1)**.

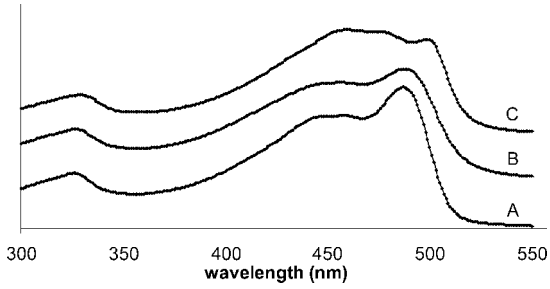


Figure 12. UV−vis spectra of polymer films: (A) **RnPPE(12/6)**; (B) **RgPPE(12/6)**; (C) **PPE(12)**.

The solid-state spectra of the PPEs were investigated using films prepared by drop-casting a solution of the polymer in $CHCl_3$ onto quartz slides followed by annealing at 120 °C for 24 h. The absorptions of the solid state films are broader and red-shifted relative to the solution spectra. This is expected on the basis of the influence of interactions between the conjugated backbones in the solid state that are absent in solution. The effect of regioregularity on the appearance of the spectra is most pronounced in the analogues of **PPE(12/1)**. The regioregular analogue (Figure 11B) has a greater contribution at higher wavelength than the regiorandom analogue (Figure 11A). This may be ascribed to the ordered arrangement of the side chains in regioregular **RgPPE(12/1)** which leads to a more planar, more conjugated conformation that packs more closely in the solid state. The irregular placement of the substituents in the regiorandom analogue impedes the formation of an ordered assembly, thereby leading to conformational disorder, a decrease in conjugation length, and weaker chain−chain interactions. This effect is not observed in the case of **PPE(12/6)** where the substituents are more similar: The regioregular (Rg) (Figure 12B) and regiorandom (Rn) analogue (Figure 12A) have almost identical UV−vis absorption spectra. The spectra of these analogues are similar to that of the symmetrical, and thereby inherently "regioregular", **PPE(12)** analogue (Figure 12C). These results suggest that regioregularity has a stronger influence on the electronic properties of PPEs substituted with dissimilar side chains (C1 and C12) system than those bearing more similar side chains (C6 and C12) or an identical pair (C12).

Molecular Assembly. X-ray diffraction studies were performed on the regiorandom and regioregular polymers to explore the effect of the relative placement of side chain on chain packing in the solid state. Experiments were conducted on thin films formed by drop-casting xylene solutions of the polymer onto a silicon substrate. The X-ray experiments were run on both pristine and annealed samples (24 h at 120 °C, under N_2).

The X-ray diffractograms of **PPE(12/6)** regioisomers (regiorandom, Figure 13A; regioregular, Figure 13B) both show a peak at $2\theta = 4.46°$ (19.9 Å) and a small peak at ~8.7° (10.2 Å). For comparison, the diffractogram for the symmetrical **PPE(12)** material shows four peaks at $2\theta = 3.54°$, 7.0°, 10.45°, and 17.45°. These can be assigned as the (100), (200), (300), and (500) planes of a lamella crystal with an interlayer spacing of 24.9 Å.[32] The strong peaks for [*h*,0,0] reflections when *h* is even, and weak peaks associated with the reflections when *h* is odd, can be interpreted as arising from an electron density within the unit cell consisting of planes with high electron density (i.e., the conjugated backbone) and low electron density (alkyl regions). Thus, by analogy, we assign the two diffraction peaks (one strong, one weak) in each of the **PPE(12/6)** materials to the (100) and (200) planes of a lamella structure with interlayer spacing of 19.9 Å (Figure 13 inset). The irregular placement of side chains would suggest that they are more likely interdigitated, and there is shorter-range order than in symmetrically substituted **PPE(12)**. Thus, as expected, the combination of hexyl and dodecyl side chains results in a smaller interlayer spacing than is observed for **PPE(12)**. The broader diffraction peaks for the regiorandom **Rg(12/6)** analogue might indicate the presence of less order than for the regioregular analogue (width at half-height for the (100) peak: **Rg**, 0.45°; **Rn**, 0.64°).

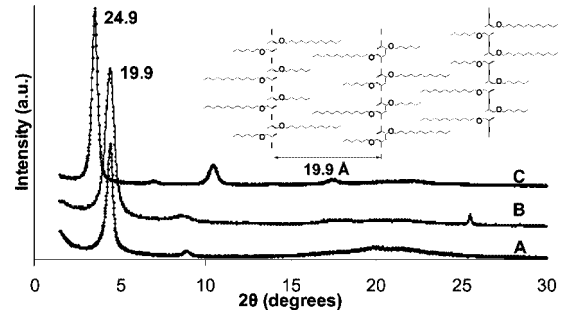


Figure 13. X-ray diffraction of annealed polymer films (annealed at 120 °C for 24 h): (A) regiorandom **RnPPE(12/6)**; (B) regioregular **RgPPE(12/6)**; (C) **PPE(12)**.

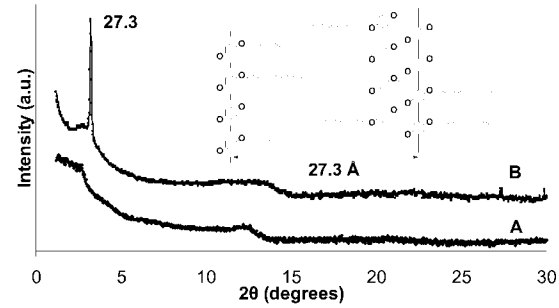


Figure 14. X-ray diffraction of annealed polymer films (annealed at 120 °C for 24 h): (A) regiorandom **RnPPE(12/1)**; (B) regioregular **RgPPE(12/1)**.

The X-ray diffractograms of the regioregular and regiorandom **PPE(12/1)** analogues are shown in Figure 14. The regioregular analogue, **RgPPE(12/1)** (Figure 14B), shows an intense and sharp first-order reflection at a *d* spacing of 27.3 Å while the regiorandom analogue is featureless (Figure 14A). The absence of higher order reflections in the diffractogram of the regioregular polymer indicates that the although this material packs in an orderly fashion, this ordering is relatively short-range. The diffractogram of the regiorandom analogue remains largely unchanged even after extensive annealing. The *d* spacing value of 27.3 Å for the **RgPPE(12/1)** homologue is *larger* than observed for the analogues with longer side chains, **PPE(12)** and **RgPPE(12/6)**, and larger than the width of the polymer ribbon transverse to the polymer chain (i.e., with the side chains in an extended all-trans conformation, Figure 14 inset). This suggests the formation of a bilayer type arrangement that would

arise from segregation of the dodecyloxy side chains and methoxy substituents on different sides of the aromatic backbone.

The bilayer packing arises from segregation of the two types of side chain. This effect, which is not observed for the **PPE(12/6)** analogues, might arise from the optimization of intramolecular packing of dodecyloxy side chain on adjacent repeating units and intermolecular interaction of these side chain in packing together the molecular ribbons. A similar assembly has been reported by Suzuki and co-workers for a regioregularly substituted poly(1,4-phenylene vinylene).[8]

Conclusion

In conclusion, we have presented strategies for the synthesis of structurally homogeneous regioregular unsymmetrically substituted poly(1,4-phenylene ethynylene)s, PPEs, by polymerization of unsymmetrically substituted 2,5-dialkoxy-4-iodophenylacetylenes. We have shown that control over the relative placement of substituents has an influence on molecular assembly and electronic structure of the PPE materials. The effect of regioregularity on the properties of unsymmetrically substituted PPEs is greatest when there is a large difference between the side chains. Expanding the choice of side chains should afford a further level of control over the molecular packing and orientation of conjugated polymer chains, which is paramount in the design of new materials for electronic and optical devices. Further work is currently underway to apply this approach to the development of polymers with distinctly different side chains (e.g., alkyl, fluoroalkyl, oligo(ethylene glycol)). This will allow for the examination of the influence of polymer microstructure and organization on the electronic and optical properties of materials in thin film devices.

Experimental Section

General Methods. All reagents were purchased from commercial sources and used without further purification unless stated. THF and Et_2O were dried over sodium benzophenone ketyl prior to distillation under nitrogen. Column chromatography was performed on flash grade silica (32−60 Å, Sorbent Technologies, Atlanta, GA). Thin-layer chromatography was performed on 3 × 5 cm silica gel plates (0.2 mm thick, 60 F254) on an aluminum support (Sorbent Technologies). NMR analysis was performed on a Bruker DSX 400 or DSX 300 instruments. Chemical shifts are reported relative to internal tetramethylsilane. IR analyses were performed on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Ultraviolet−visible analysis was performed on a Shimadzu UV-2401PC spectrometer, and fluorescence spectroscopy was performed on a Shimadzu RF-5301PC spectrofluorophotometer. The X-ray diffraction data were obtained using a Scintag X1 diffractometer equipped with copper tube and a Peltier cooled solid-state detector.

Illustrative experimental procedures are provided below for the synthesis of the iodo−ethynyl A−B type monomer **11a** for the preparation of regioregular PPEs together with spectral data for homologues **b**. Synthetic procedures for the preparation of monomers **1** and **2** for the preparation of regiorandom analogues are well-precedented and appear in the Supporting Information.

4-Methoxyphenyl *p*-Toluenesulfonate, 4a. Pyridine (15.80 g, 200 mmol) was added to a solution of 4-methoxyphenol (24.85 g, 200 mmol) and *p*-toluenesulfonyl chloride (38.15 g, 200 mmol) in dry THF (100 mL), and the mixture was stirred for 18 h at room temperature. The solution was washed with H_2O (2 × 100 mL) and dried over $MgSO_4$, and the solvent was removed under low pressure. The crude solid obtained was filtered and recrystallized from methanol to yield tosylate **4a** (45.3 g, 81.4% yield) as a white solid; mp 71−72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, $^3J_{TosH2-TosH3}$ = 8.4 Hz, 2H, tosyl-H), 7.27 (d, $^3J_{TosH3-TosH2}$ = 8.4 Hz, 2H, tosyl-H), 6.87 (d, $^3J_{ArH2-ArH3}$ = 9.2 Hz, 2H, Ar C2, 6-H), 6.75 (d, $^3J_{ArH2-ArH3}$ = 9.2 Hz, 2H, Ar C3,5-H), 3.75 (s, 3H, $-OCHH_3$), 2.44 (s, 3H, tosyl $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.13 (Ar C4), 146.39 (Ar C1), 143.86 (tosylate C1), 133.06 (tosylate C4), 130.54, 129.23 (tosylate C2,3,5,6), 124.06, 115.21 (Ar C2,3,5,6), 56.32 ($-O-CH_3$), 22.19 (tosylate $-CH_3$). IR (υ, cm^{-1}): 2971, 2931 (Ar C−H str), 2903, 2840, 1591, 1498, 1456, 1442, 1383, 1345, 1309, 1293, 1248 (C−O str), 1194, 1166, 1147, 1090, 1022, 1008, 849, 837, 815, 678, 544, 531. HRMS: calcd for $C_{14}H_{14}O_4S$ = 278.061 28, obsd = 278.061 43, Δ = 4.6 ppm.

4-Dodecyloxyphenyl *p*-Toluenesulfonate, 4b. 89% yield; pale brown solid; mp 28−29 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, $^3J_{TosH2-TosH3}$ = 8.4 Hz, 2H, tosyl-H), 7.29 (d, $^3J_{TosH3-TosH2}$ = 8.6 Hz, 2H, tosyl-H), 6.85 (d, $^3J_{ArH2-ArH3}$ = 9.1 Hz, 2H, Ar C2,6-H), 6.7 (d, $^3J_{ArH2-ArH3}$ = 9.1 Hz, 2H, Ar C3,5-H), 3.87 (t, ^3J_H = 6.5 Hz, 2H, $-OCHH_2$-), 2.43 (s, 3H, tosyl $-CH_3$), 1.70−1.85 (m, 2H), 1.65−1.80 (m, 18H), 0.87 (t, $^3J_{H11-H12}$ = 6.7 Hz, 3H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.71 (Ar C1), 145.78 (Ar C4), 145.13 (tosylate C1), 132.25 (tosylate C4), 129.61, 128.27 (tosylate C2,3,5,6), 123.19, 114.85 (Ar C2,3,5,6), 68.26 ($-O-CH_2-$), 31.84, 29.58, 29.56, 29.52, 29.49, 29.37, 29.30, 29.28, 29.10, 25.92, 22.61, 14.05. IR (υ, cm^{-1}): 2921 (Ar C−H str), 2851, 1596, 1500, 1467, 1373, 1295, 1248 (C−O str), 1195, 1168, 1152, 1092, 1008, 865, 835, 811. HRMS: calcd for $C_{25}H_{36}O_4S$ = 432.233 43, obsd = 432.235 21, Δ = 2.0 ppm.

3-Iodo-4-methoxyphenyl *p*-Toluenesulfonate, 5a. Tosylate **4a** (38.05 g, 136.87 mmol) was added to a stirred mixture of I_2 (27.80 g, 109.45 mmol), sulfuric acid (5 mL), CCl_4 (27 mL), water (32 mL), and acetic acid (65 mL). KIO_3 (11.72 g, 54.77 mmol) was added, and the mixture was heated at reflux for 48 h. The reaction was cooled to room temperature, and chloroform (70 mL) was added. The solution was washed with saturated aqueous Na_2SO_3 (200 mL) followed by 10% (w/w) aqueous NaOH (2 × 200 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a brown solid. The residue was recrystallized from methanol to give iodide **5a** (50.02 g, 90.6% yield) as a white solid; mp 84−85 °C. ^{1}H NMR: δ 7.68 (d, $^3J_{TosH2-TosH3}$ = 8.4 Hz, 2H, tosyl Ar−H), 7.34−7.37 (m, 3H, tosyl 2H and Ar C2−H), 6.93 (dd, $^3J_{ArH6-ArH5}$ = 8.9 Hz, $^4J_{ArH6-ArH2}$ = 2.8 Hz, 1H, Ar C6−H), 6.72 (d, $^3J_{ArH5-ArH6}$ = 9.0 Hz, 1H, Ar C5−H), 3.83 (s, 3H, $-OCHH_3$), 2.45 (s, 3H, tosyl $-CH_3$). ^{13}C NMR: δ 158.01 (Ar C4), 146.71 (Ar C1), 143.83 (tosylate C1), 133.92 (tosylate C4), 132.69, 130.64 (tosylate C2,3,5,6), 129.27, 124.01, 111.33 (Ar C2,6,5), 85.6 (Ar C3), 57.5 ($-O-CH_3$), 22.23 (tosylate $-CH_3$). IR (υ, cm^{-1}): 3098, 2975, 2948 (Ar C−H str), 2843, 2364, 2159, 2022, 1595, 1578, 1478, 1450, 1439, 1392, 1381, 1289, 1267 (C−O str), 1179, 1156, 1120, 1088, 1040, 1016, 872. HRMS: calcd for $C_{14}H_{13}I_1O_4S$ = 403.957 93, obsd = 403.956 92, Δ = 2.7 ppm.

4-Dodecyloxy-3-iodophenyl *p*-Toluenesulfonate, 5b. 71% yield; viscous, brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, $^3J_{TosH2-TosH3}$ = 8.4 Hz, 2H, tosyl Ar−H), 7.29−7.34 (m, 3H, 2 tosyl H, 1 Ar C2−H), 6.92 (dd, $^3J_{ArH6-ArH5}$ = 8.9 Hz, $^4J_{ArH6-ArH2}$ = 2.8 Hz, 1H, Ar C6−H), 6.64 (d, $^3J_{ArH2-ArH3}$ = 8.9 Hz, 1H, Ar C5−H), 3.94 (t, $^3J_{H1-H2}$ = 6.37 Hz, 2H, $-OCHH_2-$), 2.45 (s, 3H, tosyl $-CH_3$), 1.54−1.58 (m, 2H), 1.1−1.6 (m, 18H), 0.87 (t, $^3J_{H11-H12}$ = 6.7 Hz, 3H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.54 (Ar C4), 145.45 (Ar C1), 142.76 (tosyl C1), 133 (tosyl C4), 131.96, 129.72 (tosyl C2,3,5,6), 128.51, 123.07, 111.25 (Ar C−H), 85.61 (Ar C−I), 69.61 ($-O-CH_2-$), 31.86, 29.59, 29.52, 29.49, 29.3, 29.22, 29.15, 28.94, 25.97, 22.64, 21.67, 14.08. IR (υ, cm^{-1}): 2920 (Ar C−H str), 2850, 1596, 1577, 1482, 1464, 1375, 1288, 1262 (C−O str), 1193, 1179, 1160, 1092, 1035, 877, 810. HRMS: calcd for $C_{25}H_{35}O_4SI$ = 558.130 08; obsd = 558.125 39, Δ = 8.4 ppm.

3-Iodo-4-methoxyphenol, 6a. A solution of monoiodinated tosylate **5a** (15.00 g, 37.04 mmol) in *t*-butanol (20 mL) was bubbled with argon for 20 min. A degassed solution of 20% aqueous NaOH (20 mL) was added under argon, and the mixture was heated at reflux for 24 h. The reaction mixture was cooled and washed with 10% HCl (50 mL) followed by H_2O (2 × 100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography (CH_2Cl_2) to afford

phenol **6a** (7.49 g, 80.61% yield) as a white solid; mp 105−106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, $^4J_{ArH2-ArH6}$ = 2.9 Hz, 1H, aromatic C2−H), 6.81 (dd, $^3J_{ArH5-ArH6}$ = 8.8 Hz, $^4J_{ArH2-ArH6}$ = 2.9 Hz, 1H, Ar C6−H), 6.73 (d, $^3J_{ArH5-ArH6}$ = 8.8 Hz, 1H, Ar C5−H), 4.83 (bs, 1H, OH), 3.78 (s, 3H, −$OCHH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.64, 150.95 (Ar C1,4), 126.95 (Ar C2), 116.78 (Ar C6), 112.67 (Ar C5), 86.50 (Ar C3), 57.72 (−O−CH_3). IR (υ, cm^{-1}): 3174 (O−H), 3058, 3013, 2965, 2943, 2910 (Ar C−H str), 2838, 2662, 1583, 1485, 1453, 1431, 1277, 1266, 1240, 1205 (C−O str), 1184, 1150, 1140, 1129, 1043, 1012, 919, 877, 861, 598, 138, 698, 664, 570, 556. HRMS: calcd for $C_7H_7O_2I$ = 249.949 08, obsd = 249.951 23, Δ = 3.8 ppm.

4-Dodecyloxy-3-iodophenol, 6b. 88% yield; pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, $^4J_{ArH2-ArH6}$ = 2.89 Hz, 1H, Ar C2−H), 6.78 (dd, $^3J_{ArH5-ArH6}$ = 8.8 Hz, $^4J_{ArH2-ArH6}$ = 2.9 Hz, 1H, Ar C6−H), 6.68 (d, $^3J_{ArH5-ArH6}$ = 8.8 Hz, 1H, Ar C5−H), 6.0−6.25 (bs, 1H, OH), 3.92 (t, $^3J_{H1-H2}$ = 6.4 Hz, 2H, −$OCHH_2$−), 1.73−1.85 (m, 2H), 1.2−1.6 (m, 18H), 0.89 (t, $^3J_{H11-H12}$ = 6.6 Hz, 3H, −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.45, 150.38 (Ar C1,4), 126.4 (Ar C2), 116.33 (Ar C6), 113.8 (Ar C5), 87.3 (Ar C3), 70.68 (−O−CH_2−), 32.19, 29.94, 29.92, 29.87, 29.85, 29.63, 29.6, 29.51, 26.34, 22.97, 14.4. IR (υ, cm^{-1}): 3348 (O−H), 2920 (Ar C−H str), 2850, 1701, 1600, 1583, 1487, 1465, 1434, 1388, 1377, 1273, 1206 (C−O str), 1145, 1033, 1008, 906, 861, 799, 779. HRMS: calcd for $C_{18}H_{29}O_2I$ = 404.121 23, obsd = 404.121 55, Δ = 0.8 ppm.

4-Dodecyloxy-2-iodoanisole, 7a. NaH (60% dispersion in oil, 191 mg, 4.8 mmol) was added slowly to a solution of monoiodinated phenol **6a** (1.00 g, 3.98 mmol) in dry THF (50 mL), and the mixture was stirred for 15 min. 1-Bromododecane (1.19 g, 4.8 mmol) was added dropwise by syringe, and the reaction mixture was heated at reflux for 12 h. The mixture was cooled and diluted with water (50 mL) and then extracted with $CHCl_3$ (2 × 100 mL). The solution was dried over $MgSO_4$, and the solvent was removed under low pressure to give a pale yellow oil. The residue was subjected to flash chromatography (25:75 v/v CH_2Cl_2/hexane) to afford **7a** (360 mg, 21.6% yield) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, $^4J_{ArH3-ArH5}$ = 2.8 Hz, 1H, Ar C3−H), 6.85 (dd, $^3J_{ArH5-ArH6}$ = 8.9 Hz, $^4J_{ArH3-ArH5}$ = 2.8 Hz, 1H, Ar C5−H), 6.74 (d, $^3J_{ArH5-ArH6}$ = 8.9 Hz, 1H, Ar C6−H), 3.88 (t, $^3J_{H1-H2}$ = 5.4 Hz, 2H, −$OCHH_2$−), 3.82 (s, 3H, −$OCHH_3$), 1.68−1.80 (m, 2H), 1.40−1.52 (m, 18H), 0.86 (t, $^3J_{H11-H12}$ = 6.1 Hz, 3H, −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.78, 152.50 (Ar C1,4), 125.50, 115.30, 111.51 (Ar C3,5,6), 85.94 (Ar C2), 68.82 (−O−CH_2−), 56.93 (−O−CH_3), 31.89, 29.54, 29.31, 29.22, 25.97, 22.65, 14.11. IR (υ, cm^{-1}): 2920 (Ar C−H str), 2851, 2372, 2348, 2326, 1622, 1616, 1600, 1569, 1575, 1549, 1542, 1467, 1437, 1419, 1393, 1269, 1210 (C−O str), 1180, 1151, 1047, 1013, 921, 864, 843, 800, 748, 721, 664, 551. HRMS: calcd for $C_{19}H_{31}O_2I$ = 418.136 88, obsd = 418.141 06, Δ = 3.6 ppm.

1-Dodecyloxy-4-hexyloxy-2-iodobenzene, 7b. Monoiodinated phenol, **6b** (2.55 g, 6.30 mmol), was added to a stirred solution of PPh_3 (1.65 g, 7.55 mmol) and 1-hexanol (0.80 mL, 7.6 mmol) in Et_2O (40 mL) under Ar. Diethyl azodicarboxylate (DEAD) (1.15 mL, 7.55 mmol) was added dropwise by syringe, and the resulting pale yellow solution was stirred at room temperature for 24 h. Et_2O (60 mL) was added, and the solution was washed with 10% aqueous NaOH (200 mL) followed by H_2O (100 mL). The solution was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (20:80 v/v ethyl acetate:hexanes) to afford **7b** (2.80 g, 91% yield), pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, $^4J_{HH}$ = 2.90 Hz, 1H, Ar C3−H), 6.83 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz, 1H, Ar C5−H), 6.71 (d, $^3J_{HH}$ = 8.9 Hz, 1H, Ar C6−H), 3.93 (t, $^3J_{HH}$ = 6.4 Hz, 2H, −$OCHH_2$−), 3.87 (t, $^3J_{HH}$ = 5.4 Hz, 2H, −CH_2−), 1.65−1.85 (m, 4H), 1.20−1.58 (m, 24H), 0.84−0.94 (m, 6H, 2 × −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 153.97 (Ar C−O), 125.55, 115.62, 113.30 (Ar C−H), 87.22 (Ar C−I), 70.39, 69.05 (−O−CH_2−), 31.91, 31.59, 29.66, 29.62, 29.42, 29.34, 29.26, 26.01, 25.67, 22.68, 22.62, 14.11, 14.06. IR (υ, cm^{-1}): 2920 (Ar C−H str), 2851, 2030, 1733, 1597, 1568, 1486, 1466, 1387, 1350, 1271, 1209 (C−O str), 1106, 1062, 935, 850, 801, 770, 721. HRMS: calcd for $C_{24}H_{41}O_2I$ = 488.215 13, obsd = 488.217 04, Δ = 3.9 ppm.

2-Dodecyloxy-4-iodo-5-methoxyacetophenone, 8. Monoiodinated diether **7a** (720 mg, 1.72 mmol) was dissolved in dry CH_2Cl_2 followed by the addition of acetyl chloride (148.52 mg, 1.89 mmol), and the solution was cooled to 0 °C. $AlCl_3$ (251.63 mg, 1.89 mmol) was added in two parts to the above solution under nitrogen, and the mixture was then allowed to warm to room temperature and stir for 2 h. The reaction was quenched by pouring it into a 1:10 w/w mixture of ice/concentrated HCl. The organics was extracted with dichloromethane (2 × 50 mL) and dried over $MgSO_4$, and the solvent was removed under low pressure to yield a crude solid. The residue was purified by recrystallization from hexane to afford acetophenone **8** (450 mg, 89.5%) as a yellow solid; mp = 110−111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (s, 1H, Ar C3−H), 7.22 (s, 1H, Ar C6−H), 4.07 (t, $^3J_{HH}$ = 6.5 Hz, 2H, −$OCHH_2$−), 3.85 (s, 3H, −$OCHH_3$), 2.60 (s, 3H, −$COCH_3$), 1.75−1.88 (m, 2H), 1.18−1.56 (m, 18H), 0.80−0.92 (t, $^3J_{HH}$ = 6.2 Hz, 3H, −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.5 (−C═O), 156.6 (Ar C2), 150.7 (Ar C5), 129.5, 119.0 (Ar C1,3), 109.9 (Ar C6), 97.8 (Ar C4), 57.1 (−O−CH_2−), 26.6. IR (υ, cm^{-1}): 2946, 2915, 2868, 2846 (Ar C−H str), 1659 (C═O str), 1586, 1556, 1482, 1463, 1375, 1266, 1207 (C−O str), 1171, 1075, 1041, 1023, 1001, 986, 908, 867, 841, 795, 731, 721, 696, 599. HRMS: calcd for $C_9H_9O_3I$ = 460.147 44, obsd = 460.147 45, Δ = 2.6 ppm.

Negishi−Tour Procedure To Prepare 4-Dodecyloxy-5-ethynyl-2-iodoanisole, 11a. A solution of LDA in THF (0.17 g, 1.55 mmol) was added dropwise to a solution of acetophenone **8** (0.68 g, 1.5 mmol) in dry THF (40 mL) at 0 °C. The resulting yellow solution was stirred for 15 min, and diethyl chlorophosphate (267 mg, 1.55 mmol) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 3 h. The solution was cooled to 0 °C, and a solution of LDA in THF (0.365 g, 3.325 mmol) was added. The mixture was stirred for 3 h, and H_2O (5 mL) was added. The mixture was extracted with EtOAc, and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure to give yellow oil. The residue was subjected to column chromatography (10:90 v/v ethyl acetate/hexanes) to afford ethyne **11a** (200 mg, 30.5% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (s, 1H, Ar C3−H), 6.88 (s, 1H, Ar C6−H), 3.97 (t, $^3J_{HH}$ = 6.6 Hz, 2H, −$OCHH_2$−), 3.82 (s, 3H, −$OCHH_3$), 3.31 (s, 1H, ≡C−H), 1.74−1.84 (m, 2H), 1.20−1.58 (m, 18H), 0.88 (t, $^3J_{HH}$ = 6.6 Hz, 3H, −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.21 (Ar C4), 152.50 (Ar C1), 124.62 (Ar C3), 115.82 (Ar C6), 112.90 (Ar C5), 87.46 (Ar C2), 81.77, 79.70 (−C≡C−), 70.27 (−O−CH_2−), 57.05 (−O−CH_3), 37.16, 31.87, 29.53, 29.29, 25.88, 22.59, 13.96. IR (υ, cm^{-1}): 3289 (≡C−H str), 2920 (Ar C−H str), 2850, 2372, 2348, 2326, 1516, 1463, 1368, 1269, 1214 (C−O str), 1140, 1045, 911, 857, 811, 733, 703, 672, 617, 604. HRMS: calcd for $C_{21}H_{31}O_2I$ = 442.136 88, obsd = 442.130 23, Δ = 4.9 ppm. Elemental analysis: theoretical = C 57.02%, H 7.06%, O 7.23%; found = C 57.37%, H 7.18%, O 7.58%.

5-Dodecyloxy-2-hexyloxy-4-iodobenzaldehyde, 12. $TiCl_4$ (11.7 g, 61.4 mmol) was added dropwise to a solution of monoiodinated diether **7b** (5.0 g, 10 mmol) in dry CH_2Cl_2 (50 mL) at −40 °C in a dry flask under Ar. The mixture was stirred for 15 min at −40 °C, and dichloromethyl methyl ether (2.35 g, 20.5 mmol) was added dropwise and stirring was continued for another 2 h. The reaction mixture was poured into mixture of concentrated HCl and ice. The mixture was extracted with CH_2Cl_2 (100 mL), and the extract was washed with water (100 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (silica gel, 30% CH_2Cl_2/hexanes) afforded **12** as a white solid (2.91 g, 55% yield); mp = 57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.40 (s, 1H, −CHO), 7.43 (s, 1H, Ar C3−H), 7.16 (s, 1H, Ar C6−H), 3.95−4.02 (m, 4H, −$OCHH_2$−), 1.77−1.81 (m, 4H), 1.24−1.44 (m, 24H), 0.85−0.88 (m, 6H, 2 × −CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.28 (−CHO), 155.77 (Ar C2), 152.12 (Ar C5), 125.11 (Ar C1), 124.51 (Ar C3), 108.81

(Ar C6), 96.78 (Ar C4), 69.90, 69.44 ($-O-CH_2-$), 31.90, 31.45, 29.63, 29.56, 29.54, 29.34, 29.26, 29.04, 29.00, 26.02, 25.66, 22.68, 22.54, 14.12, 14.00. IR (υ, cm^{-1}): 2912 (Ar C−H str), 2847, 1670 (C═O str), 1587, 1458, 1383, 1213 (C−O str), 1032, 867, 827, 748, 715, 611. HRMS: calcd for $C_{25}H_{41}O_3I$ = 516.208 93, obsd = 516.205 92, Δ = 5.8 ppm.

Bestman Homologation To Prepare 1-Dodecyloxy-5-ethynyl-4-hexyloxy-2-iodobenzene, 11b. Bestman−Ohiro reagent, $CH_3COC(=N_2)PO(CH_3O)_2$ (0.45 g, 2.3 mmol), was added dropwise to a mixture of aldehyde **12** (0.5 g, 0.9 mmol) and K_2CO_3 (0.19 g, 1.4 mmol) in 12 mL of a 1:5 v/v mixture of anhydrous CH_2Cl_2 and MeOH under argon, and the mixture was stirred for 10 h. The solvent was removed under reduced pressure to obtain a pale yellow residue which was recrystallized from isopropanol to give ethyne **11b** (0.22 g, 49% yield) as a white solid; mp = 39−41 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, 1H, Ar C3−H), 6.86 (s, 1H, Ar C6−H), 3.92−3.95 (m, 4H, $-OCHH_2$), 3.29 (s, 1H, −C≡C−H), 1.76−1.81 (m, 4H), 1.26−1.48 (m, 24H) 0.85−0.92 (m, 6H, 2 × $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.81 (Ar C4), 151.65 (Ar C1), 123.73 (Ar C3), 116.64 (Ar C6), 112.19 (Ar C5), 88.28 (Ar C2), 81.74, 79.64 (−C≡C−), 70.04, 69.83($-O-CH_2-$), 31.90, 31.46, 29.62, 29.56, 29.33, 29.27, 29.10, 29.04, 26.02, 25.52, 22.68, 22.54, 14.11, 13.99. IR (υ, cm^{-1}): 3269 (C−H str), 2953 (Ar−H str), 2914, 2845, 2091 (C≡C str), 1473, 1465, 1371, 1209 (C−O str), 1026, 856, 818, 725, 687, 642. HRMS: calcd for $C_{26}H_{41}O_2I$ = 512.214 02, obsd = 512.2139, Δ = 1.0 ppm. Elemental analysis: theoretical: C, 60.93%; H, 8.06%; I, 24.76; O, 6.24%; found: C, 60.92%; H, 7.94%; I, 24.61%; O, 6.29%.

Regiorandom Dodecyloxy/Methoxy, RnPPE(12/1). The syntheses of monomers **1** and **2** are provided in the Supporting Information. A solution of monomers **1a** (379 mg, 718 μmol) and **2a** (251 mg, 718 μmol), $Pd(PPh_3)_4$ (40.2 mg, 34.9 μmol), and CuI (8.0 mg, 40 μmol) in a mixture of morpholine (16 mL) and diisopropylamine (4 mL) was heated at 70 °C for 4 days. The mixture was poured into 50 mL of acetone, and the precipitated solid was removed by filtration. The solid was then subjected to sequential extractions in a Soxhlet extractor with MeOH, acetone, and hexanes, followed by $CHCl_3$. The solvent was removed from the $CHCl_3$ fraction, and the residue (380 mg, 79% yield) was characterized. GPC (THF, UV−vis detector): 18.1 kDa, PDI = 3.7. NMR: see discussion. IR (υ, cm^{-1}): 2918, 2849, 1511, 1494, 1413, 1387, 1274, 1212, 1030, 862, 720.

Regiorandom Dodecyloxy/Hexyloxy, RnPPE(12/6). A solution of monomers **1b** (500 mg, 814 μmol) and **2b** (345 mg, 838 μmol), $Pd(PPh_3)_4$ (47.2 mg, 34.9 μmol), and CuI (10 mg, 42 μmol) in a mixture of morpholine (16 mL) and diisopropylamine (4 mL) was heated at 70 °C for 4 days. Work-up according to the procedure described above for **RnPPE(12/1)** gave **RnPPE(12/6)** as a yellow-orange solid (412 mg, 60% yield). GPC (THF, UV−vis detector): 37.8 kDa, PDI = 3.7. NMR: see discussion. IR (υ, cm^{-1}): 2918, 2849, 1511, 1494, 1413, 1387, 1274, 1212, 1030, 862, 720.

Regioregular Dodecyloxy/Methoxy, RgPPE(12/1). A−B type monomer **11a** (300 mg, 677 μmol) was treated with $Pd(PPh_3)_4$ (37.3 mg, 33.6 μmol) and CuI (7 mg, 36.8 μmol) in morpholine/diisopropylamine as described above. Precipitation and extraction as described above for **RnPPE(12/1)** gave a $CHCl_3$-soluble fraction (150 mg, 70% yield) that was characterized further. GPC (THF, UV−vis detector): 11.56 kDa, PDI = 2.5. NMR: see discussion. IR (AT-IR, neat): 2918, 2849, 1511, 1494, 1413, 1386, 1275, 1211, 1030, 859, 720.

Regioregular Dodecyloxy/Hexyloxy, RgPPE(12/6). A solution of monomer **11b** (428 mg, 0.84 mmol), toluene (10 mL), and diisopropylamine (2 mL) were added to a 50 mL flask and degassed via freeze/pump/thaw. $Pd(PPh_3)_4$ (50.0 mg, 0.86 mmol) and CuI (8.0 mg, 0.84 mmol) were added to the solution. The mixture was stirred at 60 °C for 2 days. Precipitation from MeOH and sequential extractions in a Soxhlet extractor with acetone, hexanes, and chloroform gave a chloroform fraction as an orange solid (261 mg, 81% yield). GPC (THF, UV−vis detector): 15.12 kDa NMR: see discussion. IR (AT-IR, neat): 2920, 2852, 2370, 1514, 1428, 1388, 1277, 1213, 1045, 858, 725.

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Supporting Information Available: Synthesis of monomers **1** and **2**, an alternate approach for synthesis of 4-iodophenylacetylene monomer **11a** by regioselective Friedel−Crafts acylation of dialkoxybenezene and regioselective dealkylation, and analysis of the mixture of products formed by formylation of **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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