Synthesis of Regioregular Poly(*p*-phenylenevinylene)s by Horner Reaction and Their Regioregularity Characterization

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ABSTRACT: A new synthetic route was developed to obtain highly regioregular poly[(2-methoxy-5-alkyloxy)-1,4-phenylenevinylene]s (PPVs) by the Horner reaction using asymmetrically functionalized monomers. The polymers showed good solubility in chlorobenzene at over 100 °C. The high regioregularity of the polymers was confirmed by ^{1}H NMR quantitative analysis using chlorobenzene-d_5 as solvent, which was developed for the first time in this study. Assignment of the ^{1}H NMR peaks was conducted by synthesizing four novel model compounds for PPV. UV−vis, fluorescence spectra, and XRD data revealed that these regioregular PPVs have higher crystallinity compared to regiorandom PPVs in the solid state.

Introduction

The regioregularity of conjugated polymers is well-known to be an important factor for determining their higher order structures in the solid state, such as crystallinity and molecular orientation. Crystalline packing of the regioregular polymers provides intra- and intermolecular ordering of the conjugating polymer chains in the films, leading to enhanced light absorptions and higher charge mobilities desirable for various optoelectronic device applications including organic field effect transistors and photovoltaic devices. In this sense, poly(3-alkylthiophene) (P3AT) has been researched extensively as a good example showing the importance of polymer regioregularity. Highly regioregular P3ATs synthesized in a purely "head-to-tail" coupling manner show a crystalline nature in the films, resulting in higher charge mobilities[1,2] and improved photovoltaic properties[3] compared to the regiorandom, therefore amorphous, P3ATs.

Poly[(2-methoxy-5-alkyloxy)-1,4-phenylenevinylene]s (PPVs) such as poly[(2-methoxy-5-(3′,7′-dimethyloctyloxy))-1,4-phenylenevinylene] (MDMO−PPV) and poly[(2-methoxy-5-(2′-ethylhexyloxy))-1,4-phenylenevinylene] (MEH−PPV) are another p-type semiconducting polymer commonly used for light emitting diodes[4−6] and photovoltaic devices.[7−13] Since these PPVs have two types of coupling manner similar to P3AT, they possess degrees of regioregularity in terms of the direction of the alkyloxy substitution projecting from the conjugating main chains. However, few reports have reported in the control of their regioregularity thus far.[14,15] Vanderzande et al. developed the synthesis of nonionic precursor polymers and their subsequent conversion to PPVs.[16] In their report, two isomers of asymmetric monosulfinyl chloromethylbenzenes were synthesized and used as monomers for the synthesis of the precursor polymer of MDMO−PPV. Mixtures of the isomers with 50:50 ratios were polymerized and converted to high molecular weight MDMO−PPVs.[17] They also reported the synthesis of fully regioregular MDMO−PPVs by the precursor route using only one of the isomers. Unfortunately, the fully regioregular MDMO−PPVs seems to have poor solubility in common solvents, preventing further characterization and the device application of the polymers. Later, the same group and Mozer et al. synthesized regiospecific PPVs with various regioregularities by copolymerization of the two monomers with various mixing ratios. They reported the synthesis of a regiospecific MDMO−PPV with the monomer ratio of 70:30 and their application to polymer photovoltaic devices.[18] In their report, the regiospecific PPVs showed higher hole mobility compared to a regiorandom PPV, resulting in a higher efficiency of the photovoltaic device. Considering these reports, the physical properties and device application of the fully regioregular PPVs are attractive subjects if the solubility issue can be overcome. In addition, quantitative methods to evaluate the degree of regioregularity in PPVs are necessary to further elucidate the relationship between the regioregularity and the optoelectronic properties of the polymer in the solid state. These analytical methods, however, have not been reported so far.

It is also known that properties of the PPVs strongly depend on the synthetic routes adopted. There are several common routes to synthesize these PPVs: the dehydrohalogenation reaction of bis(halogenomethyl)benzenes (Gilch route),[19,20] synthesis of ionic or nonionic precursor polymers and subsequent conjugation (the precursor routes),[21,22] and polycondensation reaction between benzylphosphonate and aldehyde (Horner route).[23,24] The PPVs synthesized by the Gilch route have relatively poor solubility because of gel formation or structural defects formed by various side reactions and incomplete elimination of the leaving groups.[25] The precursor routes also suffer from the formation of similar structural defects, although these issues could be reduced by using nonionic monomers and by changing the elimination conditions.[26] On the other hand, compared to the Gilch route, the Horner route produces all-*trans*, linear, and less defective structures of the polymers, resulting in the suppression of gel formation to give better solubility and processability into thin films.[27] Therefore, regioregular synthesis of the PPVs by the Horner route has the advantage of producing solution processable polymers with high crystallinity in the solid state.

We present here a new route to synthesize regioregular PPVs by the Horner reaction. We have synthesized novel asymmetrically functionalized monomers for the reaction and successfully obtained highly regioregular PPVs that are soluble in chlorobenzene at high temperature. In addition, we have demonstrated for the first time that the regioregularity of PPVs can be

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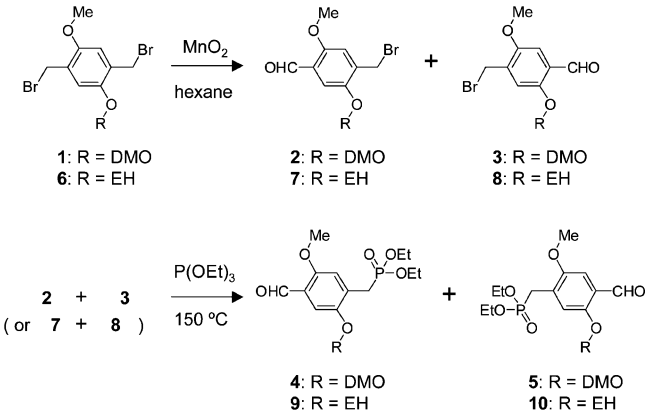
Scheme 1. Synthetic Route for Asymmetric Monomers by the Horner Reaction (DMO: 3,7-dimethyloctyl, EH: 2-ethylhexyl)



quantitatively characterized by ^{1}H NMR measurements in chlobenzene-d_5 solution.

Results and Discussion

Monomer Synthesis and Polymerization. Scheme 1 shows the synthetic route for the asymmetrically functionalized monomers. The key step of the monomer synthesis is the oxidation of one of the bromomethyl groups of the common monomers used for the Gilch route synthesis (**1** and **6**). This enabled us to synthesize the dialkoxybenzenes with both bromomethyl and aldehyde groups as a mixture of two isomers (**2** and **3**). Goswami et al. reported the selective oxidation of one of the bromomethyl groups in *p*-bis(bromomethyl)benzene by using MnO_2.[28] We applied their reaction condition to oxidize the compound **1**. As a result, the mixture of **2** and **3** was obtained in 32% yield after purification by column chromatography. The ratio of the compound **2** and **3** in the mixture was determined by ^{1}H NMR to be within a range from 2:1 to 4:1, depending on the batch. This preferred selectivity of the reaction position close to the methoxy group could be explained by the steric effect of the bulky 3,7-dimethyloctyloxy side chain, since the oxidation by MnO_2 involves the adsorption of the bromomethyl groups on the catalyst surface.

After oxidation, triethylphosphite was used to obtain the corresponding phosphonates. After this step, separation of two isomers (**4** and **5**) was possible by SiO_2 column chromatography. The yields after purification were 56% and 24% for **4** and **5**, respectively, reflecting the selectivity of the previous reaction. The monomers for MEH−PPV (**9** and **10**) were synthesized by the same reaction scheme. Regioregular MDMO−PPV (**13**) and MEH−PPV (**15**) were synthesized by adding a THF solution of *t*-BuOK to solutions of monomer **4** or **9**, respectively, at room temperature (Scheme 2). Note that, from the reaction scheme, only the regioregular PPV could be formed. As for a control, a regiorandom MDMO−PPV (**14**) was synthesized by a polycondensation reaction using the dialdehyde (**11**) and the diphosphonate (**12**) under similar reaction conditions.

Polymer Solubility. Regiorandom MDMO−PPV **14** is quite soluble in common solvents such as $CHCl_3$, THF, and toluene at room temperature. In contrast, MDMO−PPV, **13**, and MEH−PPV, **15**, are insoluble in all these solvents. The polymers **13** and **15** showed low solubility in chlorobenzene, dichlorobenzene, and trichlorobenzene at room temperature, but good solubility (more than 8 g L^{-1}) at over 100 °C. This striking difference in solubility implies high regioregularity of polymers **13** and **15**. Also, the solubility of polymers **13** and **15** at high-temperature enables us to conduct solution state characterizations and film preparation.

Scheme 2. Synthetic Route for Regioregular (13 and 15) and Regiorandom (14) PPVs (DMO: 3,7-dimethyloctyl, EH: 2-ethylhexyl)

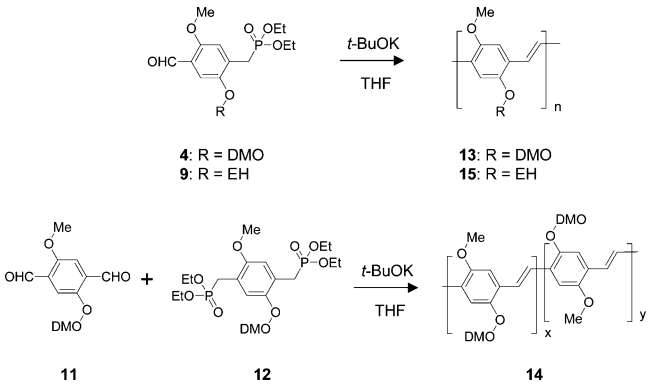


Table 1. Average Molecular Weights and Polydispersities of Synthesized PPVs Measured by GPC (Eluent: Dichlorobenzene, 140 °C)

	M_n	M_w	M_w/M_n
13	21 000	46 000	2.3
14	33 000	78 000	2.3
15	7100	13 000	1.8

Molecular Weight. The molecular weights of synthesized PPVs were measured by gel permeation chromatography (GPC) and the results are summarized in Table 1. For all the polymers, chromatographs were obtained at 140 °C using dichlorobenzene as eluent and polystyrenes as standards. The regioregular PPVs **13** and **15** have relatively low molecular weights (M_n of 21000 and 7100, respectively) compared to the regiorandom MDMO−PPV **14** (M_n of 33000). This could be attributed to the low solubility of regioregular polymers **13** and **15** in THF resulting in termination of the polymerization, since precipitation of the polymers was observed at a later stage of the reaction.

^{1}H NMR Study of the Polymers. ^{1}H NMR spectra of the polymers were measured in chlorobenzene-d_5 at 100 °C. From the NMR spectra, well-defined structures of the linear PPVs were confirmed in both the MDMO−PPVs **13** and **14** (see Supporting Information for the whole spectra). The signals observed around 7.3−7.9 ppm and 3.8−4.3 ppm could be assigned to the sp^2 CH (originating from the phenylene and the vinylene formed by the polymerization) and to the sp^3 CH (originating from $-OCH_2$ and $-OCH_3$), respectively. The integration ratio between these two regions was 4:5.3 for both polymers, which is close to the theoretical value (4:5). Combined with the FT-IR spectra of the polymers (see below), it was concluded that well-defined, *all-trans* PPVs were formed in the synthesis of both **13** and **14**.[23] Interestingly, the signals around 3.8 ppm assigned to the methoxy groups showed very different patterns between MDMO−PPVs **13** and **14** (Figure 1). Polymer **13** showed a single peak with a chemical shift of 3.75 ppm, indicating a homogeneous environment around the methoxy groups in the chlorobenzene solution. Considering the reaction scheme, this peak could be assigned to a "regioregular environment" shown as structure **c** in Figure 2. In contrast, polymer **14** shows four separated peaks with chemical shifts of 3.85, 3.82, 3.75, and 3.73 ppm. Similar splitting of the methoxy peaks was also observed for **14** in toluene-d_8. We assume that this splitting reflects four different situations around the methoxy group in relation to the neighboring side chains, as shown in Figure 2. Note that this splitting was less significant in $CDCl_3$ solution, and the methoxy signal of the polymer **14** separated into two peaks at 3.96 and 3.94 ppm (see Supporting Information). This could indicate that the aromatic molecules solvating

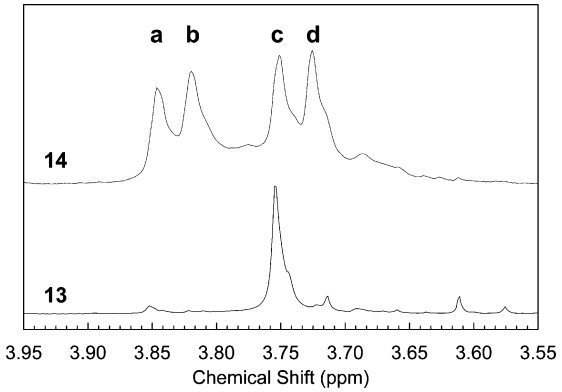
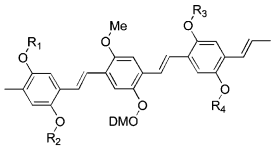


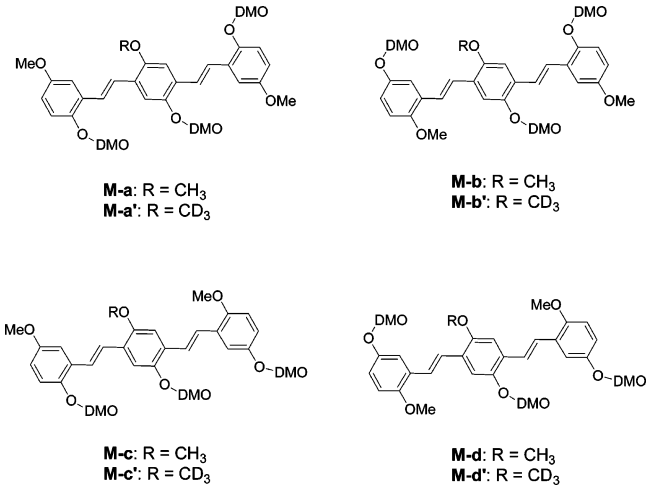
Figure 1. Methoxy region of ^{1}H NMR spectra of the MDMO−PPVs **14** (top) and **13** (bottom).



	R_1	R_2	R_3	R_4
a	Me	DMO	DMO	Me
b	DMO	Me	DMO	Me
c	Me	DMO	Me	DMO
d	DMO	Me	Me	DMO

Figure 2. Schematic representation of four possible environments for the methoxy group (top) and assignment of the four peaks (**a**-**d**) in Figure 1 determined by model compound study (bottom).

Scheme 3. Chemical Structures of Model Compounds for MDMO−PPVs to Assign the Methoxy Peaks in ^{1}H NMR Spectra



the polymer in the solution enhanced the difference of the shielding effects on the central methoxy groups. The dependence of this effect on the coupling manner might be related to the difference in steric hindrance around the methoxy groups caused by the neighboring long alkoxyl chains.

Model Compounds for PPVs. To support this hypothesis, we synthesized four model compounds (**M-a** to **-d** in Scheme 3) for the purpose of assigning these four methoxy peaks of polymer **14**. A synthetic scheme for these model compounds is presented in Scheme 4. **M-a** and **-d** were synthesized by reacting **12** using 2 equiv of one of the isomers of 2,5-dialkyloxybenzaldehyde (**16** or **18**). Since **M-b** and **-c** cannot be synthesized by the same approach, a mixture of the four isomers was synthesized statistically by using a 1:1 mixture of **16** and **18**.

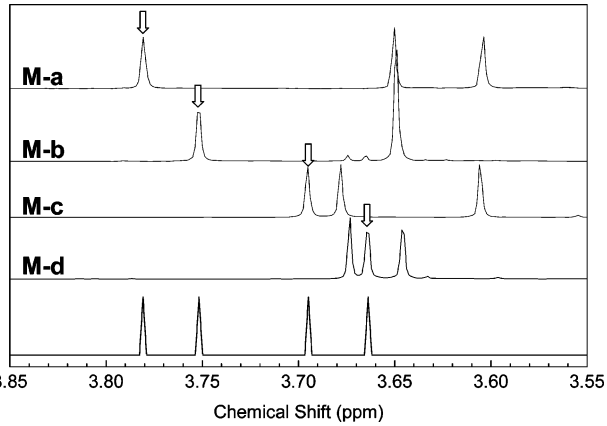
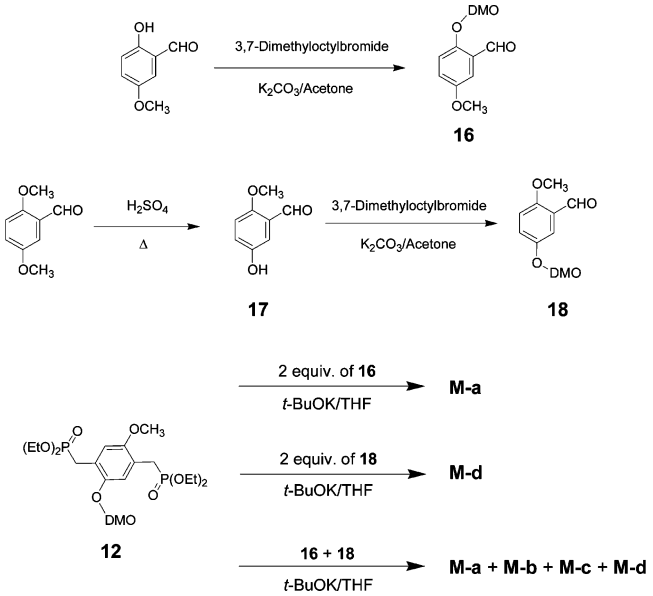


Figure 3. ^{1}H NMR methoxy region of model compounds **M-a** to **-d** measured in chlorobenzene-d_5 at 100 °C. Each arrow indicates the methoxy protons in the center. Bottom: reproduced spectrum from the four peaks indicated by the arrows.

Scheme 4. Synthetic Route for Model Compounds (M-a to d) for MDMO−PPVs



M-b and **-c** were separated by SiO_2 chromatography and PTLC. The methoxy region in the ^{1}H NMR spectra of these model compounds measured in chlorobenzene-d_5 at 100 °C is shown in Figure 3. There are three methoxy signals for each spectrum (two overlapping signals at 3.65 ppm in compound **M-b**). We also synthesized deuterized model compounds in which the central methoxy groups were replaced by $-OCD_3$ to assign the peaks in the spectra (**M-a′** to **-d′** in Scheme 3). The ^{1}H NMR of **M-a′** to **-d′** were compared to the corresponding model compounds **M-a to -d**, respectively (see Supporting Information). The signals indicated by arrows in Figure 3 disappeared in the spectra of the corresponding deuterized compounds, by which we could assign the central methoxy signals in each model compound. From these chemical shifts of the model compounds (δ 3.78, 3.75, 3.69, and 3.66 ppm for **M-a** to **-d**, respectively), we can essentially reproduce the splitting pattern of polymer **14** with an offset of about −0.08 ppm (the bottom pattern in Figure 3). Therefore, we concluded that the splitting of the methoxy signals in the regiorandom MDMO−PPV **13** reflected the different environment caused by the coupling manners. The peaks **a**−**d** in Figure 1 were assigned as shown in Figure 2. To our knowledge, this is the first report of the regioregular characterization of MDMO−PPVs by ^{1}H NMR in

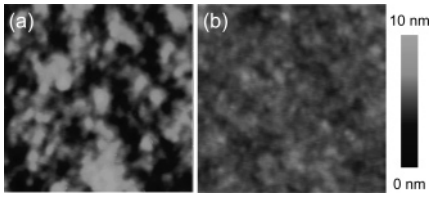


Figure 4. Atomic force microscopy (AFM) height images of spin-coated films of (a) the regioregular MDMO−PPV **13** and (b) the regiorandom MDMO−PPV **14**. Image size: 1 μm × 1 μm.

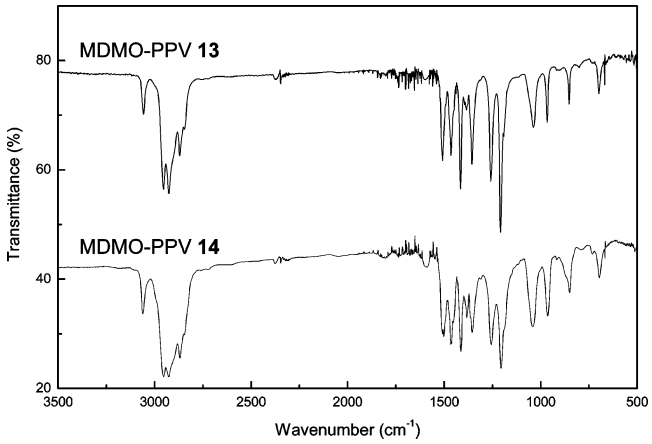


Figure 5. FT-IR spectra of the regioregular MDMO−PPV **13** (top) and the regiorandom MDMO−PPV **14** (bottom) measured using polymer films on KBr plates.

solution. At the same time, the highly regioregular structure of MDMO−PPV **13** was proven by this assignment.

The splitting pattern of the methoxy peaks of **14** in $CDCl_3$ could also be reproduced by using the same model compounds. The chemical shifts of the methoxy peaks of **M-a** to **-d** in $CDCl_3$ were 3.899, 3.900, 3.915, and 3.911 ppm, which reproduced the broad doublet pattern of **14** with an offset of about −0.06 ppm (see Supporting Information). This matching further supports the validity of the characterization by the model compounds. The splitting of the methoxy peaks into four peaks in chlorobenzene-d_5 was also observed in the case of MEH−PPVs and a similar assignment of peaks is possible.

Properties in the Solid State. The solubility at high temperature of MDMO−PPV **13** enables us to investigate the optoelectronic properties of the highly regioregular polymer both in solution and in films. We could prepare spin-cast films of the regioregular MDMO−PPV **13** from hot chlorobenzene solution (see Experimental Section). To check the film quality, the surface of the films was analyzed by atomic force microscopy (AFM). A smooth, uniform surface with a maximum surface roughness of around 10 nm was observed in the height images of both **13** and **14** films (Figure 4, parts a and b, respectively), indicating good processability of the regioregular polymer.

IR spectra of **13** and **14** in film state show an almost identical pattern, and the peaks coincide with those previously reported for MEH−PPV (Figure 5).[29] As for the characteristic peaks of the vinylene part, C−H stretching vibrations and C−H out of plane vibrations of *trans*-vinylene were observed at 3057 and 966 cm^{-1} for **13** and 3061 and 965 cm^{-1} for **14**, respectively.[29] However, the regiorandom **14** shows significant broadening of the peaks compared to the regioregular **13**, suggesting a more nonhomogeneous structure of the polymer. This could be attributed to either a slight difference in the vibration energy caused by the regiorandom nature of the polymer or an amorphous structure of the film providing the polymer with various local environments.

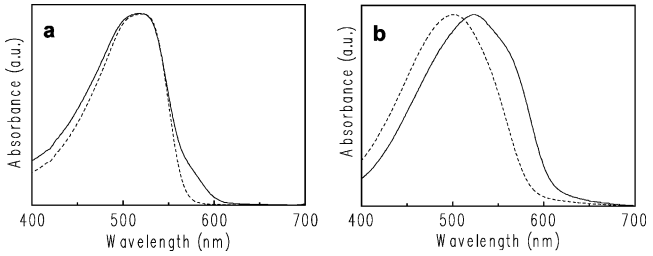


Figure 6. UV−vis spectra of MDMO−PPVs **13** (solid line) and **14** (dashed line) (a) in chlorobenzene solution at 0 °C and (b) spin-coated films on glass substrates.

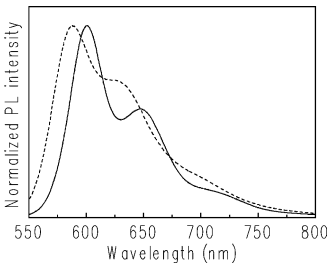


Figure 7. Fluorescence spectra of spin- coated films of **13** (solid line) and **14** (dashed line) (λ_{ex} = 500 nm).

UV−vis absorption spectra of polymer **13** and **14** in chlorobenzene solution at 100 °C gave almost identical curves with absorption maxima of 488 nm (not shown). This indicates that the regioregularity does not affect the optoelectronics properties and the conformation of the polymer chains in solutions. After the samples were cooled to 0 °C, both samples showed a red shift of the absorption maxima to 510 nm (Figure 6a). At the same time, a shoulder absorption appeared in the regioregular PPV **13** around 580 nm, which was not observed in the regiorandom PPV **14**. This might be attributed to the partial aggregation of polymer chains in the solution of PPV **13**. A similar trend was observed in the previous reports by Mozer et al. when the monomer feed ratio for the precursor polymer was changed from 70:30 to 80:20 to increase the crystallinity of the resulting PPV.[18] To investigate the effect of regioregularity in a situation with strong intermolecular interactions, UV−vis measurements on spin-coated films were conducted (Figure 6b). The film of the regiorandom **14** has a peak maximum of 503 nm, which is similar to the reported value for the MDMO−PPVs synthesized by other routes.[17] On the other hand, the regioregular **13** shows a redshift of the peak top to 528 nm and an additional absorption shoulder around 580 nm. It is concluded that the red shift and the absorption shoulder could reflect the elongation of conjugated length and better $\pi-\pi$ stacking of the polymer chains due to the higher crystallinity of the polymer **13** in the film. This type of spectral change is similar to the one observed for highly regioregular P3AT upon crystallization.[30] Fluorescence spectra also show a similar redshift of the emission maximum for polymer **13** (600 nm) compared to **14** (580 nm) in films upon monochromatic excitation at 500 nm (Figure 7). This could be attributed to emission from the extended polymer chains with longer conjugation length and/or from the crystalline parts in the films of **13** with smaller energy gaps.

Differential scanning calorimetry (DSC) measurements of the polymers were conducted. The regiorandom **14** showed T_g of 35 °C and no melting point (The reported T_g values of regiorandom MDMO−PPVs are in the range of 45−80 °C depending on the reports).[17,31,32] In contrast, no thermal transition

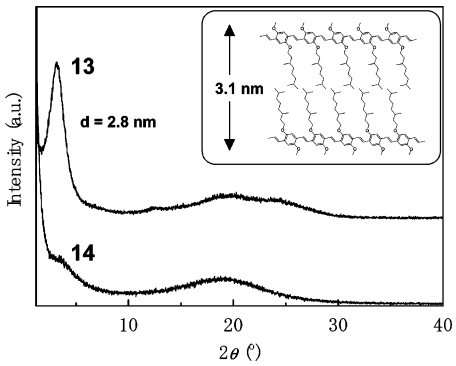


Figure 8. X-ray diffraction patterns of MDMO−PPVs **13** and **14** in solid state; inset: possible alignment of polymer **13** in solid state.

was observed in the regioregular **13** up to 250 °C. Thermal gravimetry (TG) of the polymer showed slightly better stability in **13** compared to **14**. The weight losses for **13** and **14** were 1.6% and 3.6% at 300 °C, respectively, and 11% and 17% at 350 °C, respectively.

To directly investigate the crystallinity of the polymer in the solid state, X-ray diffraction (XRD) patterns were collected on powder samples of the polymers (Figure 8). The regioregular polymer **13** has a diffraction peak at 2θ of 3.2°, corresponding to an interlayer distance of 2.8 nm. This could be attributed to the distance between the polymer backbones separated by the side chains as shown in the inset of Figure 4. From the molecular model with extended alkyl chains, the interlayer distance for the postulated structure was estimated as 2.8−3.2 nm depending on the tilting and the interdigitation of the alkyl chains. In contrast, the regiorandom PPV **14** does not show any diffraction peak, indicating the amorphous nature of the material. These properties of XRD coincide with the previous report by Mozer et al. conducted on the regioregular PPV produced by the precursor route.[33] The above results support the crystalline nature of the regioregular PPV in the solid state.

Conclusion

We have developed a new synthetic route to obtain highly regioregular PPVs by the Horner reaction. The high crystallinity and the solution processability of the polymers could be advantageous for various device applications. Measurements of basic electrical properties of the polymers and applications for photovoltaic devices are underway. We have also demonstrated for the first time that the regioregularity of PPVs can be quantitatively determined by ^{1}H NMR in chlorobenzene-d_5, which is a very straightforward, useful tool to investigate the relationship between the physical properties and regioregularity of PPVs.

Experimental Section

Synthesis. All reagents were used as received. 1,4-Bis(bromomethyl)-2-methoxy-5-(3′,7′-dimethyloctyloxy)-benzene (**1**), 1,4-bis(bromomethyl)-2-methoxy-5-(2′-ethylhexyloxy)-benzene (**6**), 2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-xylenebis (diethylphosphonate) (**12**) were synthesized by following the procedure reported previously in the paper.[23]

4-Bromomethyl-2-methoxy-5-(3′,7′-dimethyloctyloxy)benzaldehyde (2), 4-Bromomethyl-5-methoxy-2-(3′,7′-dimethyloctyloxy)benzaldehyde (3), and 2-Methoxy-5-(3′,7′-dimethyloctyloxy)-terephthalaldehyde (11). A suspension of **1** (225 mg, 0.50 mmol) and activated manganese dioxide (Aldrich, 1 g) in 10 mL of *n*-hexane was heated at 60 °C with stirring for 3 h. After cooling, the manganese dioxide was removed by filtration. The filtrate was evaporated and subjected to column chromatography (silica, CH_2Cl_2) to afford a yellow solid (**11**) (41 mg, 26%) and light yellow oil as a mixture of **2** and **3** (61 mg, 32%). The ratio of **2** and **3** in the mixture was 2:1 determined by ^{1}H NMR. Unreacted starting material was also recovered (29%).

Mixture of **2** and **3**: ^{1}H NMR (500 MHz): δ 0.86−1.88 (m, 19H), 3.90 (m, 3H), 4.06 (m, 2H), 4.53 (s, 2H), 7.01 (s, 1H), 7.31 (s, 1H), 10.42−10.44 (2s, 1H). MALDI−TOF−MS: 385.10 (calcd 384.13).

11: ^{1}H NMR (500 MHz): δ 0.86−1.89 (m, 19H), 3.94 (s, 3H), 4.10 (m, 2H), 7.45 (s, 2H), 10.50 (d, 2H). MALDI−TOF−MS: 322.15 (calcd 320.20).

[4-Formyl-5-methoxy-2-(3′,7′-dimethyloctyloxy)benzyl]phosphonic Acid Diethyl Ester (4) and [4-Formyl-2-methoxy-5-(3′,7′-dimethyloctyloxy)benzyl]phosphonic Acid Diethyl Ester (5). Triethylphosphite (0.041 mL, 0.23 mmol) was added to the mixture of **2** and **3** (61 mg, 0.16 mmol) and the mixture was heated slowly to 150 °C. After 1 h, excess triethylphosphite was removed at 150 °C in vacuum. The products were separated by column chromatography using CH_2Cl_2 and subsequently ethyl acetate as eluent. Products **4** (40 mg, 56%) and **5** (17 mg, 24%) were obtained as light yellow and orange oils, respectively.

4: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.88 (m, 25H), 3.29 (d, J = 22.6 Hz, 2H), 3.90 (s, 3H), 3.97−4.08 (m, 4H), 7.08 (d, J = 2.4 Hz, 1H), 7.30 (s, 1H), 10.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 16.33, 19.60, 22.57, 24.64, 26.56, 27.97, 29.88, 36.21, 37.25, 39.17, 56.13, 62.09, 67.23, 109.33, 115.11, 123.72, 129.48, 150.86, 156.09, 189.15. IR (film on KBr): 3466, 2955, 2929, 2869, 2762, 1682, 1613, 1498, 1467, 1418, 1393, 1367, 1322, 1285, 1256, 1214, 1165, 1112, 1098, 1053, 1030, 966, 879, 786, 696, 530 (cm^{-1}). MALDI−TOF−MS: 443.27 (calcd 442.25). Anal. Calcd for $C_{28}H_{39}O_6P$: C, 62.44; H, 8.82. Found: C, 62.22; H, 8.98.

5: ^{1}H NMR ($CDCl_3$, 500 MHz):δ 0.86−1.88 (m, 25H), 3.29 (d, J = 22.6 Hz, 2H), 3.90 (s, 3H), 4.03−4.08 (m, 4H), 7.05 (d, J = 2.4 Hz, 1H), 7.30 (s, 1H), 10.43 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 16.29, 19.57, 22.53, 24.63, 26.78, 27.92, 29.85, 36.10, 37.21, 39.16, 55.98, 62.11, 67.47, 108.26, 116.17, 123.85, 129.39, 151.20, 155.95, 189.29. IR (film on KBr): 3466, 2955, 2929, 2869, 2762, 1682, 1613, 1498, 1467, 1418, 1393, 1367, 1322, 1285, 1256, 1214, 1165, 1112, 1098, 1053, 1030, 966, 879, 786, 696, 530 (cm^{-1}). MALDI−TOF−MS: 443.37 (calcd 442.25). Anal. Calcd for $C_{28}H_{39}O_6P$: C, 62.44; H, 8.82. Found: C, 62.16; H, 8.98.

4-Bromomethyl-2-methoxy-5-(2′-ethylhexyloxy)benzaldehyde (7) and 4-Bromomethyl-5-methoxy-2-(2′-ethylhexyloxy)-benzaldehyde (8). 6 (210 mg, 0.50 mmol) and activated manganese dioxide (240 mg) were reacted and purified following the same procedure as described for **2** and **3** to yield a light yellow solid (mixture of **7** and **8**, 35 mg, 20%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90−1.78 (m, 15H), 3.93 (m, 3H), 3.95 (m, 2H), 4.53 (s, 2H), 7.01 (s, 1H), 7.31 (s, 1H), 10.42−10.46 (2s, 1H).

[4-Formyl-5-methoxy-2-(2′-ethylhexyloxy)benzyl]phosphonic Acid Diethyl Ester (9) and [4-Formyl-2-methoxy-5-(2′-ethylhexyloxy)benzyl]phosphonic Acid Diethyl Ester (10). Triethylphosphite and a mixture of **7** and **8** (0.7 g, 1.7 mmol) were reacted and purified by following the same procedure as described for **4** and **5**. Product **9** was isolated by SiO_2 chromatography as an orange liquid (0.18 g, 30%). **10** was obtained as a mixture with **9** and further purification was not attempted.

9: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90−1.78 (m, 21H), 3.30 (d, J = 22.5 Hz, 2H), 3.86 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 4.00−4.14 (m, 4H), 7.10 (d, J = 2.4 Hz, 1H), 7.29 (s, 1H), 10.41 (s, 1H).

Regioregular Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (13). Phosphonate **4** (38 mg, 0.086 mmol) was dissolved in anhydrous THF (1 mL) under N_2. A 1 M solution of *t*-BuOK in anhydrous THF (Aldrich, 0.13 mL, 0.13 mmol) was added dropwise to the mixture. After the addition, the mixture was stirred for 24 h at room temperature. The reaction was quenched by pouring the solution into a mixture of methanol and chloroform (2:1 volume ratio). Precipitated polymer was collected by filtration. The polymer was purified by reprecipitation from hot chlorobenzene

solution to acetone and collected by filtration and dried under vacuum. A dark red fibrous solid was obtained (21 mg, 84%).

^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C): δ 0.88−2.07 (m, 19H), 3.88 (s, 3H), 4.29 (s, 2H), 7.45−7.89 (m, 4H). IR (film on KBr): 3057 (*trans*-vinylene C−H str), 2954, 2926, 2869, 2845, 1507, 1465, 1415, 1383, 1356, 1258, 1207, 1038, 966 (*trans*-vinylene C−H out of plane bend), 853, 698 (cm^{-1}). See Supporting Information for ^{1}H NMR and IR spectra.

Regiorandom Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (14). Dialdehyde **11** (68 mg, 0.12 mmol) and diphosphonate **12** (38 mg, 0.12 mmol) were dissolved in anhydrous THF (1.0 mL) under N_2. A solution of *t*-BuOK in anhydrous THF (Aldrich, 0.18 mL, 1.0 M, 0.18 mmol) was added in one portion. After the addition, the mixture was stirred for 35 h at room temperature. The reaction was quenched by pouring into a mixture of methanol and chloroform (2:1 ratio), and the polymer was collected by filtration. The polymer was purified by reprecipitation from chloroform to acetone and collected by filtration. The collected red fiber was dried under vacuum (53 mg, 77%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.84−1.98 (m, 19H), 3.95 (d, 3H), 4.12 (m, 2H), 7.18−7.51 (m, 4H). ^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C): δ 0.88−2.07 (m, 19H), 3.86−3.98 (q, 3H), 4.22−4.29 (d, 2H), 7.39−7.90 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 20.12, 22.71, 25.09, 28.26, 30.82, 37.27, 37.95, 39.75, 56.43, 68.66, 110.26, 110.64, 111.97, 124.48, 128.71, 152.17, 152.24, 152.67. IR (film on KBr): 3061 (*trans*-vinylene C−H str), 2954, 2927, 2869, 2846, 1509, 1503, 1467, 1464, 1455, 1415, 1384, 1356, 1312, 1258, 1207, 1043, 965 (*trans*-vinylene C−H out of plane bend), 852, 697 (cm^{-1}). See Supporting Information for ^{1}H NMR and IR spectra.

Regioregular Poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (15). The monomer **9** was reacted by following the same procedure as for polymer **13**.

^{1}H NMR (C_6D_5Cl, 500 MHz): δ 1.05−2.01 (m, 15H), 3.87 (s, 3H), 4.19 (s, 2H), 7.40−7.96 (m, 4H).

2-(3′,7′-Dimethyloctyloxy)-5-methoxybenzaldehyde (16). 2-Hydroxy-5-methoxybenzaldehyde (0.61, 4 mmol), 3,7-dimethyloctyl bromide (1.33 g, 6 mmol) and K_2CO_3 (0.83 g, 6 mmol) were dissolved in dried acetone (50 mL) and the mixture was refluxed for 48 h. The precipitate was separated by filtration and the filtrate was concentrated by evaporation and subjected to SiO_2 column chromatography ($CHCl_3$/hexane) to give the product as a clear liquid (0.28 g, 24%).

^{1}H NMR ($CDCl_3$): δ 0.86−1.89 (m, 19H), 3.80 (s, 3H, −O*CH*$_3$), 4.07 (m, 2H, −O*CH*$_2$−), 6.95 (d, J = 9.1 Hz, 1H), 7.12 (dd, J_a = 9.1 Hz, J_b = 3.6 Hz, 1H), 7.32 (d, J = 3.6 Hz, 1H), 10.47 (s, 1H, −C*H*O). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.59, 156.36, 153.44, 125.05, 123.49, 114.39, 109.99, 67.48, 55.73, 39.16, 37.22, 36.10, 29.85, 27.92, 24.64, 22.54, 19.60. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.77; H, 9.89.

2-Methoxy-5-hydroxybenzaldehyde (17). The synthesis was conducted by following a reported procedure.[34] Concentrated H_2SO_4 (40 mL) was slowly added to 2,5-dimethoxybenzaldehyde (3.32 g, 20 mmol) at 0 °C. The solution was heated at 55 °C with stirring for 46 h. The reaction was quenched with water and the product was extracted first with Et_2O and then aqueous NaOH. The solution was acidified with aqueous HCl and extracted with Et_2O. The solution was dried with $MgSO_4$ and concentrated by evaporation. The crude product was subjected to SiO_2 column chromatography ($CHCl_3$/MeOH) and subsequently precipitated from MeOH/H_2O to give the product as a slightly brown solid (0.9 g, 29%).

^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H, −O*CH*$_3$), 6.57 (s, 1H, −O*H*), 6.89 (d, J = 9.2 Hz, 1H), 7.13 (dd, J_a = 9.2 Hz, J_b = 3.1 Hz, 1H), 7.37 (d, J = 3.1 Hz, 1H), 10.38 (s, 1H, −C*H*O). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.53, 156.58, 149.95, 124.82, 123.96, 113.71, 113.31, 56.14. Anal. Calcd for C_8H_8O: C, 63.15; H, 5.30. Found: C, 62.96; H, 5.43.

2-Methoxy-5-(3′,7′-dimethyloctyloxy)benzaldehyde (18). 17 (0.61 g, 4 mmol) and 3,7-dimethyloctyl bromide (1.33 g, 6 mmol) was reacted by the same procedure as described for **16**. The product was obtained as a clear liquid (0.1 g, 10%).

^{1}H NMR ($CDCl_3$): δ 0.86−1.89 (m, 19H), 3.90 (s, 3H, −O*CH*$_3$), 3.98 (m, 2H, −O*CH*$_2$−), 6.94 (d, J = 9.2 Hz, 1H), 7.12 (dd, J_a = 9.2 Hz, J_b = 3.4 Hz, 1H), 7.32 (d, J = 3.4 Hz, 1H), 10.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.58, 156.56, 153.14, 124.93, 123.96, 113.26, 111.22, 67.03, 56.13, 39.20, 37.23, 36.16, 29.81, 27.94, 24.63, 22.57, 19.60. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.81; H, 9.69.

Model Compound M-a. To a mixture of **16** (0.089 g, 0.31 mmol) and **12** (0.078 g, 0.14 mmol) in THF (10 mL) was added 1.0 M *t*-BuOK solution in THF (0.3 mL, 0.3 mmol). After the solution turned fluorescent green, the product was extracted with $CHCl_3$ and subjected to SiO_2 column chromatography ($CHCl_3$/hexane) and subsequently to PTLC (EtOAc/hexane) to give the product as a yellow oil (60 mg, 51% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 57H), 3.818 (s, 3H, −O*CH*$_3$), 3.825 (s, 3H, −O*CH*$_3$), 3.90 (s, 3H, central −O*CH*$_3$), 3.99−4.13 (m, 6H, −O*CH*$_2$−), 6.77−6.76 (m, 2H), 6.84 (d, J = 9.1 Hz, 2H), 7.15 (d, J = 2.4 Hz, 2H), 7.19−7.20 (m, 2H), 7.47 (d, 2H, J = 3.7 Hz), 7.48 (s, 2H). ^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C): δ 0.86−1.89 (m, 57H), 3.60 (s, 3H, −O*CH*$_3$), 3.65 (s, 3H, −O*CH*$_3$), 3.78 (s, 3H, central −O*CH*$_3$), 3.97−4.00 (m, 4H, −O*CH*$_2$−), 4.10−4.11 (m, 2H, −O*CH*$_2$−), 6.72 (t, J = 2.7 Hz, 1H), 6.74 (t, J = 2.4 Hz, 1H), 6.78 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 7.25 (s, 1H), 7.27 (d, J = 3.1 Hz, 1H), 7.31 (s, 1H), 7.32 (d, J = 3.1 Hz, 1H), 7.68 (d, J = 1.8 Hz, 2H), 7.70 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 19.78, 19.84, 22.56, 22.66, 24.67, 24.74, 24.76, 27.93, 27.95, 30.14, 36.48, 36.53, 37.32, 37.38, 37.48, 39.26, 55.66, 55.79, 56.21, 67.77, 67.83, 67.89, 108.97, 108.99, 110.50, 110.53, 111.28, 111.54, 113.63, 113.77, 123.15, 123.48, 123.64, 127.07, 127.29, 128.14, 128.21, 150.98, 151.02, 151.05, 151.46, 153.75, 153.77. MALDI−TOF−MS: 840.68 (calcd 840.63). Anal. Calcd for $C_{55}H_{84}O_6$: C, 78.52; H, 10.06. Found: C, 78.44; H, 10.55.

Model Compound M-d. 18 (0.129 g, 0.44 mmol) and **12** (0.113 g, 0.20 mmol) were reacted in the same manner as described above and purified by SiO_2 column chromatography ($CHCl_3$/hexane) to obtain the product as a yellow oil (60 mg, 36% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 57H), 3.85 (s, 6H, −O*CH*$_3$), 3.91 (s, 3H, central −O*CH*$_3$), 3.99 (m, 4H, −O*CH*$_2$−), 4.10 (m, 2H, −O*CH*$_2$−), 6.82−6.78 (m, 4H), 7.15 (s, 1H), 7.17 (s, 1H), 7.19 (d, J = 3.1 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 4.3 Hz, 2H), 7.46 (s, 2H). ^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C): δ 0.86−1.89 (m, 57H), 3.57 (s, 3H, −O*CH*$_3$), 3.59 (s, 3H, central −O*CH*$_3$), 3.63 (s, 3H, −O*CH*$_3$), 3.89−3.93 (m, 6H, −O*CH*$_2$−), 6.65 (d, J = 4.9 Hz, 1H), 6.67 (d, J = 5.5 Hz, 1H), 6.77 (t, J = 2.7 Hz, 2H), 6.78 (t, J = 2.7 Hz, 2H), 7.19 (s, 1H), 7.32 (s, 1H), 7.41 (t, J = 3.4 Hz, 2H), 7.77−7.78 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 19.68, 19.84, 22.57, 22.59, 22.67, 22.69, 24.66, 24.68, 27.92, 27.97, 29.85, 29.88, 30.09, 36.42, 36.55, 37.33, 37.36, 39.26, 56.28, 56.32, 56.44, 66.91, 66.95, 67.99, 109.30, 110.67, 112.23, 112.28, 112.39, 112.59, 114.18, 114.34, 123.11, 123.79, 124.09, 127.02, 127.35, 127.92, 151.17, 151.34, 151.37, 151.53, 153.35. MALDI−TOF−MS: 840.23 (calcd 840.63). Anal. Calcd for $C_{55}H_{84}O_6$: C, 78.52; H, 10.06. Found: C, 78.25; H, 10.24.

Model Compounds M-b and M-c. A mixture of **16** (0.35 g, 1.2 mmol), **18** (0.35 g, 1.2 mmol), and **12** (0.564 g, 1.0 mmol) was reacted in the same manner as described above. A mixture of four isomers (**M-a** to **M-d**) was produced. The fractions were separated by SiO_2 column chromatography (EtOAc/hexane). The first and last fractions in the column chromatography were **M-b** and **M-c**, respectively. **M-b** was further purified by PTLC ($CHCl_3$/hexane) to obtain the pure product as a yellow oil (78 mg, 37%). **M-c** was recrystallized from hexane at −15 °C to give a yellow solid (20 mg, 9.5%).

M-b: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 57H), 3.82 (s, 3H, −O*CH*$_3$), 3.85 (s, 3H, −O*CH*$_3$), 3.90 (s, 3H, central −O*CH*$_3$), 4.00 (m, 4H, −O*CH*$_2$−), 4.09 (m, 2H, −O*CH*$_2$−), 6.76−6.79 (m, 2H), 6.83 (2H, t, J = 9.5 Hz), 7.15 (1H, s), 7.17 (1H, s), 7.19 (d, 1H, J = 2.4 Hz), 7.22 (d, 1H, J = 2.4 Hz), 7.44 (2H, d, J = 4.9 Hz), 7.48 (s, 2H). ^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C):

δ 0.86−1.89 (m, 57H), 3.65 (s, 6H, −OCH_3), 3.75 (s, 3H, central −OCH_3), 3.95−4.00 (m, 4H, −OCH_2−), 4.03−4.04 (m, 2H, −OCH_2−), 6.74−6.77 (m, 4H), 7.24 (s, 1H), 7.29 (s, 1H), 7.32 (d, J = 3.1 Hz, 1H), 7.34 (d, J = 3.1 Hz, 1H), 7.67 (s, 2H), 7.70 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.69, 19.78, 19.80, 22.57, 22.60, 22.66, 22.71, 24.66, 24.75, 24.76, 27.94, 27.97, 29.83, 30.11, 30.14, 36.42, 36.43, 36.47, 36.53, 37.33, 37.38, 37.42, 39.25, 39.26, 55.66, 56.26, 56.35, 66.93, 67.82, 67.93, 108.94, 110.64, 111.23, 112.20, 112.56, 113.65, 113.75, 114.13, 123.07, 123.13, 123.62, 123.76, 126.98, 127.36, 127.89, 128.17, 150.96, 151.06, 151.31, 151.46, 153.33, 153.73. MALDI−TOF−MS: 840.68 (calcd 840.63). Anal. Calcd for $C_{55}H_{84}O_6$: C, 78.52; H, 10.06. Found: C, 78.28; H, 10.24.

M-c: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 57H), 3.83 (s, 3H, −OCH_3), 3.85 (s, 3H, −OCH_3), 3.91 (s, 3H, central −OCH_3), 3.98−4.02 (m, 4H, −OCH_2−), 4.08 (m, 2H, −OCH_2−), 6.77 (m, 2H), 6.83 (m, 2H), 7.15 (d, J = 3.7 Hz, 2H), 7.18 (d, 1H, J = 3.1 Hz), 7.20 (d, J = 3.1 Hz, 1H), 7.46 (m, 4H). ^{1}H NMR (C_6D_5Cl, 500 MHz, 100 °C): δ 0.86−1.89 (m, 57H), 3.61 (s, 3H, −OCH_3), 3.68 (s, 3H, −OCH_3), 3.70 (s, 3H, central −OCH_3), 3.96−4.01 (m, 4H, −OCH_2−), 4.08−4.09 (m, 2H, −OCH_2−), 6.72−6.73 (m, 2H), 6.77−6.79 (m, 2H), 7.19 (s, 1H), 7.27 (d, J = 3.1 Hz, 1H), 7.30 (s, 1H), 7.35 (d, J = 3.1 Hz, 1H), 7.68 (d, J = 3.1 Hz, 2H), 7.69 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.69, 19.81, 19.85, 22.58, 22.60, 22.67, 22.70, 24.68, 24.70, 27.94, 27.97, 29.89, 30.11, 30.14, 36.43, 36.46, 36.51, 36.55, 37.33, 37.37, 37.39, 39.27, 55.84, 56.29, 56.47, 66.95, 67.84, 67.93, 109.37, 110.61, 111.56, 112.28, 112.43, 113.65, 113.89, 114.33, 123.18, 123.50, 123.67, 124.10, 127.10, 127.27, 127.96, 128,17, 151.04, 151.14, 151.39, 151.52, 153.35, 153.79. MALDI−TOF−MS: 840.68 (calcd 840.63). Anal. Calcd for $C_{55}H_{84}O_6$: C, 78.52; H, 10.06. Found: C, 78.39; H, 10.31.

4-(3′,7′-dimethyloctyloxy)phenol (19). Hydroquinone (3.0 g, 27 mmol), 3,7-dimethyloctyl bromide (4.42 g, 20 mmol), and NaOH (0.8 g, 20 mmol) were dissolved in EtOH (15 mL) and the mixture was refluxed for 6 h. The mixture was poured into water and extracted with hexane. The organic layer was dried with $MgSO_4$ and the filtrate was concentrated by evaporation. The crude product was separated from the dialkoxyl byproduct by SiO_2 column chromatography ($CHCl_3$) to give the product as a clear liquid (2.12 g, 42%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 19H), 3.89−3.97 (m, 2H, −OCH_2−), 4.71 (s, 1H, −OH), 6.73−6.79 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 19.65, 22.58, 22.68, 24.64, 27.95, 29,84, 36.32, 37.29, 39.23, 67.10, 115.62, 115.99, 149.37, 153.30.

Methoxy-d_3-4-(3′,7′-dimethyloctyloxy)benzene (20). 19 (1.25 g, 5 mmol), K_2CO_3 (1.38 g, 10 mmol) and CD_3I (4.0 g, 28 mmol) were dissolved in dry MeCN in an autoclave and the mixture was heated at 90 °C for 48 h. The mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with aqueous $Na_2S_2O_3$ and dried with $MgSO_4$, and the filtrate was concentrated by evaporation. The crude product was subjected to SiO_2 column chromatography (CH_2Cl_2) to give the product as a clear liquid (1.15 g, 86%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 19H), 3.89−3.97 (m, 2H, −OCH_2−), 6.82 (d, J = 1.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 19.64, 22.58, 22.68, 24.63, 27.94, 29,81, 36.32, 37.28, 39.22, 66.91, 114.53, 115.38, 153.25, 153.61.

1,4-Bis(bromomethyl)-2-methoxy-d_3-5-(3′,7′-dimethyloctyloxy)-benzene (21). 20 (1.0 g, 2.2 mmol), paraformaldehyde (1.0 g, 33 mmol), and NaBr (1.13 g, 11 mmol) were dispersed in 10 mL of AcOH. The suspension was heated at 70 °C, and 1 mL of a mixture of AcOH and H_2SO_4 (1:1 vol) was added. After the solution was stirred at 70 °C for 1 h, it was poured into water, and the product was extracted with $CHCl_3$. The organic layer was neutralized, dried with $MgSO_4$, filtered, and concentrated by evaporation. The crude product was subjected to SiO_2 column chromatography (Hex/$CHCl_3$) to give the product as a white solid (0.237 g, 24%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 19H), 4.02 (m, 2H, −OCH_2−), 4.53 (s, 4H, −PhCH_2Br), 6.86 (s, 2H).

2-Methoxy-d_3-5-(3′,7′-dimethyloctyloxy)-1,4-xylenebis(diethylphosphonate) (22). 21 (0.2 g, 0.44 mmol) was reacted by following the same procedure as for **4**. The product was separated by SiO_2 column chromatography (EtOAc/MeOH) to give the product as a clear liquid (0.245 g, 98%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86−1.89 (m, 19H), 3.20 (d, J = 22.6 Hz, 2H, −Ar−CH_2P), 3.24 (d, J = 22.6 Hz, 2H, −ArCH_2P−), 4.02 (m, 8H, −POCH_2−), 6.90 (s, 1H), 6.93 (s, 1H).

Model Compounds M-a′ to d′. 22 (0.114 g, 0.2 mmol), **16** (0.07 g, 0.24 mmol), and **18** (0.07 g, 0.24 mmol) were reacted in a similar manner to the synthesis of **M-b** and **-c**. The fractions were separated by SiO_2 column chromatography (EtOAc/hexane). The first and last fractions in the column chromatography were **M-b′** and **-c′**, respectively. **M-a′** and **-d′** were obtained as a mixture in the middle fraction. The ^{1}H NMR patterns of each fraction were matched to the non-deuterized counterparts except for the disappearance of one of the methoxy peaks, and all the fractions were sufficiently pure to conduct the assignment of the methoxy peaks. See Supporting Information for details.

Measurements. Gel permeation chromatography (GPC) was performed on a Waters Alliance GPC 2000 system with a differential refractive index detector with TSKgel GMH_6-HT and GMH_6-HTL columns and dichlorobenzene as eluent at 140 °C. The polymer samples for GPC were reprecipitated from hot chlorobenzene/MeOH. The dichlorobenzene solution was filtered at 145 °C using a ceramic filter (pore size: 1.0 μm) before the sample injection. ^{1}H and ^{13}C NMR spectra were measured on a JEOL Alpha FT-NMR spectrometer equipped with an OXFORD superconducting magnet system (500 MHz). UV−vis and FT-IR spectra were recorded on Shimazu MPC-3100 and IRPrestige-21 systems, respectively. Fluorescence spectra were recorded on a Hitachi F-4500, using an excitation wavelength of 500 nm. X-ray diffraction (XRD) patterns were recorded on a Rigaku RCD-2400H diffractometer. Differential scanning calorimetry (DSC) and thermal gravimetry (TG) were performed on Rigaku DSC 8230 and Rigaku TG 8120, respectively, with a heating rate of 10 K min^{-1} under a N_2 flow.

Film Preparation. Films of the regiorandom MDMO−PPV (**14**) were prepared by the conventional spin-coating technique from chlorobenzene solution at room temperature. Films of the regioregular MDMO−PPV (**13**) were prepared as follows: prior to casting, the substrates and glass pipettes were heated to around 120 °C in an oven. Spinning was started immediately after the hot solution (>100 °C) of the polymer in chlorobenzene was dropped on the hot substrate by using the hot glass pipettes. The films were dried under nitrogen for 10 min.

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Supporting Information Available: Figures showing IR spectra of the monomers. ^{1}H NMR and IR spectra of the polymers and the model compounds, a synthetic scheme, ^{1}H NMR spectra for the deuterized model compounds, and GPC traces of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature (London)* **1999**, *401* (6754), 685−688.

(2) Jiang, X.; Patil, R.; Harima, Y.; Ohshita, J.; Kunai, A. *J. Phys. Chem. B* **2005**, *109*, 221−229.

(3) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S.; Ree, M. *Nat. Mater.* **2006**, *5* (3), 197−203.

(4) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403−428.
(5) Kang, I.-N.; Hwang, D.-H.; Shim, H.-K.; Zyung, T.; Kim, J.-J. *Macromolecules* **1996**, *29*, 165−9.
(6) Vissenberg, M. C. J. M.; Blom, P. W. M. *Synth. Met.* **1999**, *102*, 1053−1054.
(7) Halls, J. J. M.; Friend, R. H. *Synth. Met.* **1997**, *85*, 1307−1308.
(8) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789−91.
(9) Marks, R. N.; Halls, J. J. M.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *J. Phys.* **1994**, *6*, 1379−94.
(10) Gao, J.; Yu, G.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 692−695.
(11) Kietzke, T.; Egbe, D. A. M.; Hoerhold, H.-H.; Neher, D. *Macromolecules* **2006**, *39*, 4018−4022.
(12) Yang, X.; Van Duren, J. K. J.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J. *Macromolecules* **2004**, *37*, 2151−2158.
(13) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15−26.
(14) Pan, M.; Bao, Z. N.; Yu, L. P. *Macromolecules* **1995**, *28* (14), 5151−5153.
(15) Liu, Y. B.; Lahti, P. M.; La, F. *Polymer* **1998**, *39*, 5241−5244.
(16) Lutsen, L. J.; Van Breemen, A. J.; Kreuder, W.; Vanderzande, D. J. M.; Gelan, J. M. J. V. *Helv. Chem. Acta.* **2000**, *83*, 3113−3121.
(17) Lutsen, L.; Adriaensens, P.; Becker, H.; Van Breemen, A. J.; Vanderzande, D.; Gelan, J. *Macromolecules* **1999**, *32*, 6517−6525.
(18) Mozer, A. J.; Denk, P.; Scharber, M. C.; Neugebauer, H.; Sariciftci, N. S.; Wagner, P.; Lutsen, L.; Vanderzande, D. *J. Phys. Chem. B* **2004**, *108*, 5235−5242.
(19) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Polym. Chem.* **1966**, *4*, 1337−1349.
(20) Neef, C. J.; Ferraris, J. P. *Macromolecules* **2000**, *33*, 2311−2314.
(21) Wessling, R. A.; Zimmerman, R. G. U. S. Patent. 67−617832, 1970.
(22) McCallien, D. W. J.; Thomas, A. C.; Burn, P. L. *J. Mater. Chem.* **1999**, *9*, 847−849.
(23) Pfeiffer, S.; Horhold, H. H. *Macromol. Chem. Phys.* **1999**, *200* (8), 1870−1878.
(24) Egbe, D. A. M.; Roll, C. P.; Birckner, E.; Grummt, U.-W.; Stockmann, R.; Klemm, E. *Macromolecules* **2002**, *35*, 3825−3837.
(25) Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094−8095.
(26) Roex, H.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **2003**, *36*, 5613−5622.
(27) Holzer, W.; Penzkofer, A.; Tillmann, H.; Horhold, H. H. *Synth. Met.* **2004**, *140*, (2−3), 155−170.
(28) Goswami, S.; Jana, S.; Dey, S.; Adak, A. K. *Chem. Lett.* **2005**, *34* (2), 194−195.
(29) Voss, K. F.; Foster, C. M.; Smilowitz, L.; Mihailovic, D.; Askari, S.; Srdanov, G.; Ni, Z.; Shi, S.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1991**, *43*, 5109−5118.
(30) Brown, P. J.; Thomas, D. S.; Kohler, A.; Wilson, J. S.; Kim, J. S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B* **2003**, *67*, 064203.
(31) Bertho, S.; Haeldermans, I.; Swinnen, A.; Moons, W.; Martens, T.; Lutsen, L.; Vanderzande, D.; Manca, J.; Senes, A.; Bonfiglio, A. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 385−389.
(32) Veenstra, S. C.; Verhees, W. J. H.; Kroon, J. M.; Koetse, M. M.; Sweelssen, J.; Bastiaansen, J.; Schoo, H. F. M.; Yang, X.; Alexeev, A.; Loos, J.; Schubert, U. S.; Wienk, M. M. *Chem. Mater.* **2004**, *16*, 2503−2508.
(33) Mozer, A. J.; Denk, P.; Scharber, M. C.; Neugebauer, H.; Sariciftci, N. S.; Wagner, P.; Lutsen, L.; Vanderzande, D.; Kadashchuk, A.; Staneva, R.; Resel, R. *Synth. Met.* **2005**, *153* (1−3), 81−84.
(34) Ulrich, H.; et al. *J. Org. Chem.* **1974**, *39*, 2437.

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