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Communications to the Editor

Synthesis and Characterization of Regioregular Cyano-Substituted Poly(*p*-phenylenevinylene)

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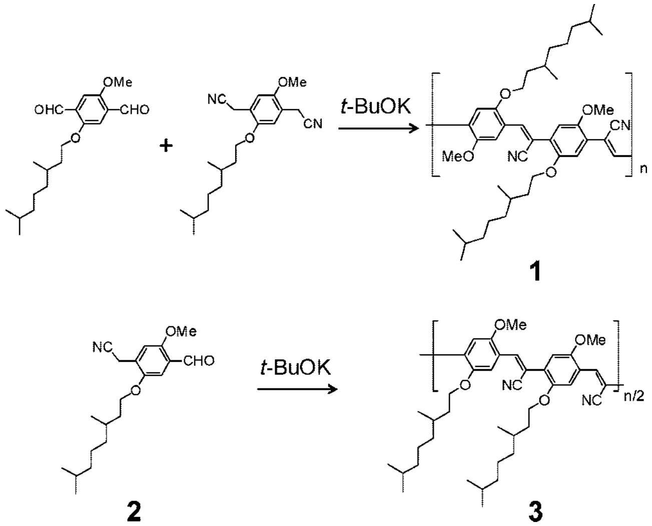
Semiconducting polymers have been attracting much interest recently for use in organic electronic devices such as photovoltaics,[1−3] field effect transistors (FETs)[4] and light-emitting diodes (LEDs).[5] Their flexibility, synthetically adjustable properties, and processability from the solutions make them promising candidates for applications to inexpensive and large area electronic devices. Among them, dialkoxy-substituted poly(*p*-phenylenevinylene) (PPV) derivatives with cyano groups on the vinylene units (CN-PPVs) are one of the examples investigated extensively as an n-type material.[6,7] CN-PPVs have higher electron affinity than PPV owing to the strong electron-withdrawing cyano groups, which enable them to accept and transport electrons. Since the variety of soluble n-type polymers is very limited, CN-PPV has attracted much attention for application to LEDs,[6] photovoltaics,[8−10] and n-channel FETs.[11] However, the relatively low electron mobility of CN-PPVs restricted device performance compared with other soluble n-type polymers[12−14] (the electron mobility of $10^{-9}-10^{-5}$ cm^2 V^{-1} s^{-1} has been reported for CN-PPVs depending on the measurement methods[11,15]). Therefore, improvement of the electron mobility in CN-PPV would lead to high performance in various polymer-based devices.

The regioregularity of conjugated polymers is one of the important factors for controlling their higher order structures in the solid state such as crystallinity, molecular orientation, and intra- and intermolecular ordering, which greatly affect the charge mobility in the film. For example, poly(3-hexylthiophene) (P3HT) shows strong dependence of hole mobility on its regioregularity, resulting from the crystallinity difference in the films.[16] Recently, we have synthesized fully regioregular poly[(2-methoxy-5-(3,7-dimethyloctyloxy))-1,4-phenylenevinylene] (MDMO-PPV) via the Horner route,[17] which was proven to have a highly ordered structure and higher hole mobility in the films compared with the regiorandom counterpart.[18] These improvement of hole mobility was one of the factors for the performance enhancement in photovoltaic devices with P3HT[19] and MDMO-PPV.[18,20]

Scheme 1. Synthetic Route for Regiorandom (1) and Regioregular (3) CN-PPVs



Therefore, it is expected that the regioregularity of CN-PPV could be an important factor for increasing the electron mobility in the film. Conventionally, soluble CN-PPV (**1**) was synthesized via alternative polycondensation of a dialdehyde and a dinitrile (Scheme 1). Since there is no selectivity in the coupling manner, the resulting CN-PPV has a regiorandom configuration in terms of the alkoxy substitutions. Although symmetrical substitution with long alkoxy groups would solve this regiorandomness,[21] it would prevent strong interchain interactions in the films as

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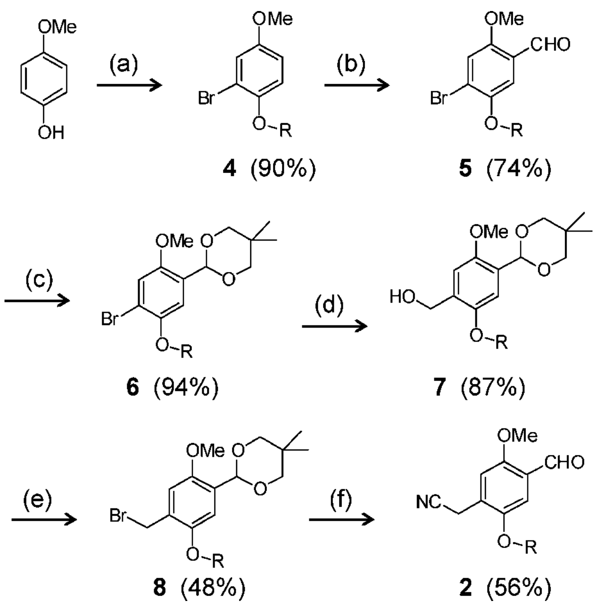
Scheme 2. Synthetic Route for the Novel Asymmetric Monomer (R = 3,7-Dimethyloctyl)[a]



[a] (a) Br_2, CH_2Cl_2, rt, then R−Br, K_2CO_3, MeCN, reflux; (b) $MeOCHCl_2$, $TiCl_4$, CH_2Cl_2, 0 °C to rt, then HCl, H_2O, rt; (c) 2,2-dimethylpropane-1,3-diol, TsOH, toluene, reflux; (d) BuLi, THF, DMF, −78 °C to rt, then $NaBH_4$, THF, 0 °C to rt; (e) PPh_3, CBr_4, THF, 0 °C to rt; (f) KCN, 18-crown-6, MeCN, H_2O, reflux, then CF_3COOH, H_2O, CH_2Cl_2, rt.

suggested by UV−vis absorption in the previous reports.[6,22,23] In addition, the alternative polycondensation creates two nonequivalent phenylene units, which makes the configuration even more complex. In contrast, polycondensation of one monomer that has both an aldehyde and a nitrile group (**2**) is expected to proceed only in the head-to-tail manner, resulting in completely regioregular CN-PPV (**3**) analogous to the regioregular synthesis of MDMO-PPV as previously reported. In this study, completely regioregular poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-1-cyanovinylene] (**3**) was synthesized for the first time, and its electronic properties were compared with the regiorandom counterpart **1**.

Scheme 2 shows the synthetic route for the asymmetrically functionalized monomer **2**. Compound **4** was prepared from *p*-methoxyphenol according to the procedures previously reported.[24,25] The key step of the monomer synthesis is the formation of the tetra-substituted benzene compound with different functionality (**5**). We found that the reaction using $TiCl_4$ and CH_3OCHCl_2[26] selectively formylate the 5-position of the compound **4** to give **5** in a moderate yield. Reaction of **5** with 2,2-dimethylpropane-1,3-diol in refluxing toluene gave the protected aldehyde (**6**).[27] **6** was treated with *n*-BuLi followed by quenching with dry DMF, reduced with $NaBH_4$, and brominated with CBr_4/PPh_3 to afford the bromide **8**, according to the reported method.[28] The monomer **2** was obtained as yellow oil by cyano substitution of **8** followed by cleavage of the acetal group with CF_3COOH.

Regioregular CN-PPV (**3**) was synthesized via Knoevenagel polycondensation of the monomer **2** (Scheme 1). The mixed solvent of THF/MeOH (6:1)[29] or toluene/*t*-BuOH (10:1)[30] were found to be the optimal reaction solvents for synthesizing soluble regioregular products. Treatment of **2** with *t*-BuOK in refluxing toluene/*t*-BuOH mixture (10:1) afforded black solid **3**, which is further studied in this report. The polymer **1** was purchased from Aldrich and purified by reprecipitation before use.

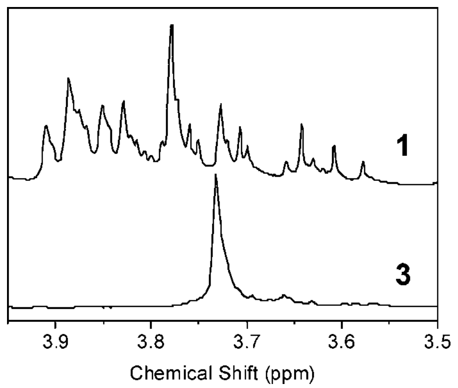


Figure 1. Methoxy region of ^1H NMR spectra of CN-PPVs **1** (top) and **3** (bottom).

FT-IR spectra (data not shown) demonstrated that the peak of the cyano groups was shifted after polymerization; the monomer **2** showed a peak at 2255 cm^{-1} assigned to $-C{\equiv}N$ stretching linked to a saturated sp^3 carbon. After the reaction, the product **3** showed one peak at 2205 cm^{-1} that could be assigned to $-C{\equiv}N$ stretching linked to a vinyl group. These results indicate the successful conversion of **2** to the polymer **3** with the conjugated cyano substitution.

The regioregularity of CN-PPVs was characterized using ^1H NMR spectra based on the assignment previously developed for MDMO-PPVs.[17] Figure 1 shows the methoxy region of the ^1H NMR spectra of CN-PPV **1** and **3** in C_6D_5Cl. Regiorandom **1** has many peaks, reflecting different environments for the methoxy groups caused by the neighboring alkoxy chains and cyano groups. In contrast, **3** has only one peak in this region, indicating that the methoxy groups exist in a highly uniform environment. We concluded that the polymer **3** has a completely regioregular structure as expected from the synthetic scheme.

There is a significant difference in solubility between **1** and **3**. Regiorandom **1** is quite soluble in $CHCl_3$, CH_2Cl_2, and THF at room temperature. On the other hand, regioregular **3** is insoluble in all these solvents at room temperature, while it dissolves in chlorobenzene or dichlorobenzene at more than 8 g L^{-1} at above 100 °C. This lower solubility of **3** implies its higher structural order in solid states. The solubility of **3** at high temperature enables us to prepare thin films by solution process.

The molecular weight of synthesized **3** was measured by gel permeation chromatography (GPC) at 140 °C using dichlorobenzene as eluent and polystyrenes as standards. **3** had relatively low molecular weight ($M_w = 13\,000$, $M_w/M_n = 1.5$), which could be attributed to the low solubility of regioregular **3** in the reaction solvent. The molecular weight of **1** was $M_w = 29\,000$ with $M_w/M_n = 4.4$ as measured by GPC at 40 °C using $CHCl_3$ as eluent.

Optical properties of the CN-PPVs in solutions and film states were also investigated. Thin films were spin-coated from hot chlorobenzene solutions. Figure 2a shows UV−vis the absorption spectra of the diluted solutions in chlorobenzene at 100 °C. **1** and **3** showed almost identical spectra with the peak top of around 455 nm, as previously reported for the CN-PPVs.[22,31] This similarity indicates that the regioregularity does not affect the average conformation of the polymer chains and the optoelectronic properties in solutions. Figure 2b shows the absorption spectra of thin films. Both the films of **1** and **3** showed largely red-shifted spectra compared with those in solutions with the absorption maxima of 509 and 564 nm, respectively, and additional absorption shoulders in the longer

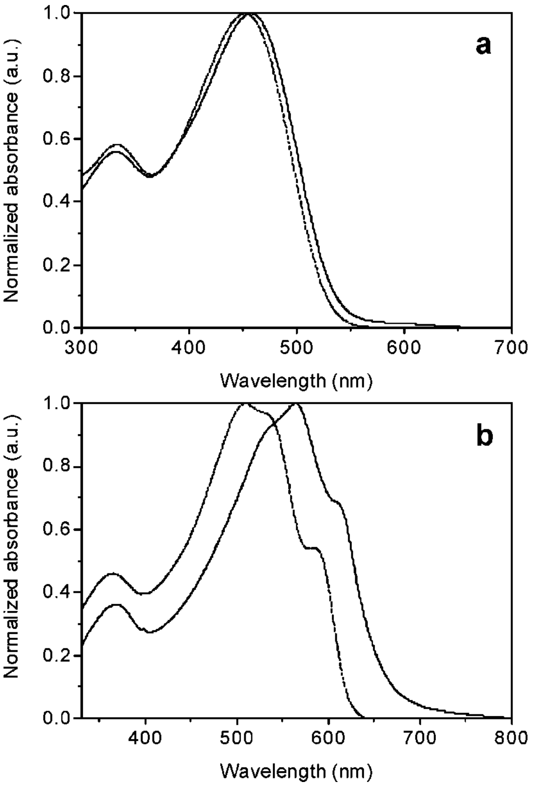


Figure 2. UV−vis spectra of CN-PPVs **1** (dotted line) and **3** (solid line): (a) chlorobenzene solution at 100 °C and (b) spin-coated films on glass substrates.

wavelength region. Regioregular CN-PPV **3** showed more drastic red shift of the absorption than regiorandom CN-PPV **1** in the films. This suggests the elongation of conjugated length and/or better $\pi-\pi$ stacking of the polymer chains due to the higher structural order of the polymer **3** in the film. This type of spectral change is similar to those observed for highly regioregular P3HT[19] and MDMO-PPV.[17,20] The degree of red shift in the film of **3** compared with the solution was about 0.5 eV, which is the largest value among various PPV derivatives. Fluorescence spectra also showed a similar red shift of the emission maximum for polymer **3** (787 nm) compared with **1** (701 nm) in films upon monochromatic excitation at the absorption maximum wavelength (see Supporting Information (SI) for the spectra). This could be attributed to the emission from the extended polymer chains with longer conjugation length and/or from the crystalline parts in the films of **3** with smaller energy gaps. This strong interchain interaction can affect the electronic properties of **3** in the films.

Electron mobility in the films of CN-PPVs was measured using the space charge limited current (SCLC) region in current−voltage measurement of the electron-only thin film devices.[32] The device structure was ITO/Cs_2CO_3/CN-PPV/Ca/Al. Cs_2CO_3 was spin-coated on ITO cathode to prevent hole injection to the organic layer as previously reported.[33] The current−voltage characteristics were measured in vacuo under dark. Both ohmic and SCLC regions were observed in the $I-V$ curves for each device, and the SCLC regions were fitted to extract the electron mobility (see SI for the details). To check the validity of the measurements, the thickness dependence of current density was investigated. The double-logarithm plot of the film thickness and the current density fitted the line reasonably well with a slope of −3 (see SI), which is indicative of an SCLC region. As a result, electron mobility of the regioregular **3** was improved by about 30 times compared with the regiorandom **1** in the film states. The electron mobilities were calculated using Child's law[34] as 5.3×10^{-7} and 1.8×10^{-5} cm^2 V^{-1} s^{-1} for the films of regiorandom and regioregular CN-PPVs, respectively. Among many possible reasons for this enhancement of electron mobility, one of the reasons could be stronger intra- or interchain ordering in the film of **3**, considering the difference in the optoelectrical properties of the films described above.

Table 1. HOMO (E_{HOMO}) and LUMO Energies (E_{LUMO}), Ionization Potentials (IPs), and Band Gaps (E_g) of CN-PPVs 1 and 3 in eV

	E_{HOMO}[a]	IP[b]	E_{LUMO}[a]	$E_{g(CV)}$[a]	$E_{g(Opt)}$[c]
1	−5.81	−5.61	−3.49	2.32	1.99
3	−5.69	−5.46	−3.54	2.15	1.88

[a] Determined from onset potentials of CV peaks based on the assumption that the Fc/Fc$^+$ redox couple is 5.15 eV[22] relative to the vacuum level. [b] Determined from onset of PYS spectra. [c] Deduced from absorption edge of UV−vis absorption spectra in film states.

To further elucidate the structures in solid state, X-ray diffraction (XRD) patterns were collected on the powder samples of the polymers. Both **1** and **3** have clear diffraction peaks with *d*-spacings of 2.05, 1.03, and 0.35 nm (see SI). The pattern can be assigned to a lamellar structure consisting of the layers of $\pi-\pi$ stacked PPV backbones that are separated by the alkyl side chains.[23] The similarity between the XRD patterns suggests the similar crystalline structures of **1** and **3** in the bulk.

Energy levels of the CN-PPVs were investigated using photoelectron yield spectroscopy (PYS), cyclic voltammetry (CV), and optical band gaps estimated from the absorption edge in the film state. The results are summarized in Table 1. The onset potentials of the oxidation peaks in CV indicate that the regioregular CN-PPV **3** has a lower oxidation potential by 0.12 V than the regiorandom **1** (see SI). Ionization potentials (IPs) of the polymer films on ITO substrate measured by PYS showed a difference of +0.15 eV between the regioregular and regiorandom CN-PPVs (see SI). Both the CV and PYS results agreed well, indicating that the HOMO level of the regioregular CN-PPV **3** is positively shifted by 0.12−0.15 eV compared with the regiorandom **1**. In contrast, LUMO levels of CN-PPVs **1** and **3** showed similar values with only a 0.05 eV difference, as determined from the onset potentials of reduction peaks in CV. The regioregular CN-PPV **3** has a 0.11−0.17 eV smaller band gap than the regiorandom **1**, as determined both from CV values and UV−vis absorption edge. These differences in the band structures of **1** and **3** could be attributed to the difference in polymer configuration in the film.[35] These results suggest that the regioregular CN-PPV **3** has strong electron acceptability similar to the regiorandom **1** together with a lower band gap. These characteristics could be advantageous for polymer photovoltaic applications.

In conclusion, regioregular CN-PPV with asymmetric substitution with methoxy and long alkoxy groups was synthesized for the first time by using a new monomer. The regioregular CN-PPV showed stronger interchain interactions in the films and higher electron mobility than the regiorandom counterpart. This regioregularity effect on the electron mobility would provide the strategy for designing new n-type polymers. Moreover, the high electron acceptability and lower band gap of the regioregular CN-PPV would make it a promising semiconducting material for various device applications.

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Supporting Information Available: Experimental details, synthetic methods, NMR, FL, CV, PYS, XRD, and SCLC. This material is available free of charge via the Internet at http://pubs.acs.org.

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