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Soluble polyphenylene homopolymers with controllable microstructure and properties: Optical and electrical characteristics of completely dehydrogenated poly(1,3-cyclohexadiene) as a π-conjugated polymer semiconductor

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Abstract

The optical and electrical characteristics of soluble polyphenylene (PPH) homopolymers obtained by the complete dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) are reported for the first time. The optical properties were strongly affected by the molar ratios of 1,2-/1,4-phenylene (Ph) units. The HOMO and LUMO energy levels were approximately −5.2 and −2.0 eV, and the microstructure did not influence those energy levels or the band gap energies. The generation of carriers (both electron and hole) in the polymer films was observed, and the drift mobility of electrons and holes was affected by the molar ratios of 1,2-/1,4-Ph units in the polymer chain. The drift mobility of electrons in PPH homopolymers with a high content of 1,4-Ph units was in the order of 10^{-4} to 10^{-5} (cm^2/Vs). The *I*–*V* characteristics of soluble PPH homopolymers were controllable by the microstructure of PPH. The 1,2-Ph unit imparted appropriate solubility and toughness to the PPH homopolymers.

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Keywords: Soluble polyphenylene; Microstructure and properties; Poly(1,3-cyclohexadiene)

1. Introduction

The study of polyphenylenes (PPHs) is one of the most interesting research subjects in polymer chemistry. In particular, poly(1,4-phenylene), a typical PPH, has been recognized as an attractive high performance material due to its thermal and chemical stability [1], electrical [2] and optoelectronic properties [3–5].

From a perspective of molecular structure, the π-orbital conjugation of PPH is regarded as the source for these properties. It has been considered that regular repetition of 1,4-phenylene (1,4-Ph) units contributes to the excellent properties of PPH, and 1,2-phenylene (1,2-Ph) units have been regarded as structural defects. Unfortunately, the degree of crystallization of the polymer chain is increased with an increase in the length of 1,4-Ph unit sequences. Poly(1,4-Ph) becomes insoluble, infusible, and intractable at more than six repeat units [1,6]. This is a major and serious problem that prevents the application of poly(1,4-Ph). Therefore, the most important challenge is to improve the solubility of PPH and so a variety of different approaches have been attempted [7–22]. Finally, the most convenient route to synthesize PPH is the dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) [9–22]. However, from all previous studies, the dehydrogenated products obtained have been insoluble polymers, partially dehydrogenated polymers, and copolymers. Therefore, the real nature of the

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PPH homopolymer has been unclear up until this time. Furthermore, the polymerization of 1,3-cyclohexadiene (1,3-CHD), a monomer of PCHD, has sometimes been reported to be difficult under various conditions, including the cases of ionic polymerization, radical polymerization, and coordination polymerization. The polymers obtained under these conditions were of low molecular weight or in low yield, and the microstructure of the polymer chain could not be controlled [9–17,23–25].

In previous papers [26–29], we reported the first successful example of living anionic polymerization of 1,3-CHD; homopolymers, copolymers, and block copolymers with narrow molecular weight distribution, controlled molecular weight and a clear polymer chain structure were successfully synthesized. Furthermore, an effective method for controlling the microstructure of the polymer chain of PCHD was reported. PCHD has a structure consisting of a main chain formed by a 1,2-addition (1,2-CHD unit) and a 1,4-addition (1,4-CHD unit). The molar ratio of 1,2-CHD/1,4-CHD units in the polymer chain can be controlled by the type and amount of amine used, and also by the use of alkyllithium as an initiator [28,30].

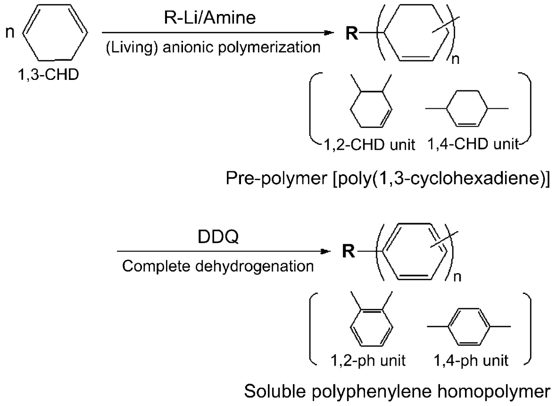
Recently, we attempted to obtain completely dehydrogenated PCHD with a controlled polymer chain consisting of 1,2-Ph and 1,4-Ph units as a new type of PPH. As a result, soluble PPH homopolymers obtained by the complete dehydrogenation of PCHD were synthesized as polar macromolecules (Scheme 1) [31].

In this paper, we report for the first time the optical and electrical characteristics of soluble PPH homopolymers obtained by the complete dehydrogenation of PCHD. The influence of the microstructure of the PPH homopolymer on these characteristics is also described.

2. Experimental section

2.1. Materials

1,3-Cyclohexadiene (1,3-CHD), cyclohexane, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were refluxed over calcium hydride (CaH_2) and then distilled under an argon atmosphere. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was dried under reduced pressure in dry argon. All other reagents were purchased from Aldrich and were used as received unless otherwise described.



Scheme 1.

2.2. General procedure for the anionic polymerization of 1,3-CHD with alkyllithium/amine systems [22,31]

A well-dried 50 mL Schlenk tube was purged with dry argon, and cyclohexane and alkyllithium (*n*-butyllithium (*n*-BuLi), 1.60 M in *n*-hexane, or *sec*-butyllithium (*s*-BuLi), 1.40 M in cyclohexane) were added at room temperature (ca. 25 °C) using hypodermic syringes. Amine (TMEDA or DABCO) was then added to this solution under a dry argon atmosphere and the mixture was stirred for 10 min. 1,3-CHD was then supplied to this solution with a hypodermic syringe, and the reaction mixture was magnetically stirred under an argon atmosphere at room temperature. After polymerization, dehydrated methanol (MeOH) was added to the reaction mixture in an equimolar amount to the amount of lithium atoms present in the reaction mixture, in order to terminate the reaction. Then, the polymerization mixture was poured into a large volume of ethanol (EtOH) to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in an argon atmosphere at room temperature for 24 h, resulting in a white powdery polymer.

2.3. General procedure for the dehydrogenation of PCHD with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [31]

PCHD powder (0.20 g, consisting of 2.50 mmol of CHD units) was placed into a 50 mL Schlenk tube and dried under reduced pressure. The Schlenk tube was alternately evacuated and filled with dry argon several times. Anhydrous 1,2-dichlorobenzene (DCBz, 20 mL) was added with a hypodermic syringe, and the mixture was stirred until the polymer was fully dissolved. DDQ (2.27 g, 10 mmol, 400% with respect to CHD units) was added under dry argon atmosphere at room temperature and the reaction mixture was magnetically stirred under an argon atmosphere at 90 °C. After dehydrogenation, the reaction mixture was poured into a large volume of isopropanol (IPA) to precipitate the polymer, which was then separated by filtration. The product was washed with an excess amount of EtOH and dried under reduced pressure in an argon atmosphere at room temperature for 24 h, resulting in a dark brown powdery polymer.

2.4. Measurements

The number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) equipped with a differential refractometer detector using a Shimadzu Shim-pack GPC-80M column at 40 °C. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene standards. ^1H NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$), tetrahydrofuran

(THF-d_8), or *N*,*N*-dimethylformamide (DMF-d_7) at 500 MHz using a JEOL JNM-LA500 spectrometer. UV/vis spectroscopic measurements were performed in THF using a JASCO V570 UV/VIS/NIR spectrometer with quartz cells. Photoluminescence (PL) spectra of the polymers were measured in THF using a JASCO FP-777 spectrofluorometer with quartz cells. The redox potential was measured by cyclic voltammetry (CV) in a one-compartment cell with a polarization unit (TOHO PS-06). The CV measurement was conducted for a cast film (1.0 mm) on a platinum (Pt) disk working electrode (1.6 mm in diameter) in dry acetonitrile (CH_3CN) containing 0.1 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as an electrolyte, under a nitrogen atmosphere and at a scanning rate of 50 mV/s. A platinum spiral wire was used as a counter electrode and Ag/AgCl as a reference electrode. The drift mobility was measured using a conventional time-of-flight (TOF) method at room temperature with a xenon flash lamp (Hamamatsu Photonics, L2359) and a digitizing oscilloscope (Gould, DSO630). The current–voltage (*I*–*V*) characteristics were measured by an electrometer (Advantest, TR-6143). Film thickness was determined with a profilometer (Dektak II, Solan).

3. Results and discussion

3.1. Synthesis of soluble polyphenylene homopolymers [31]

In order to reveal the nature of PPH, the soluble PPH homopolymers were synthesized according to the synthetic route shown in Scheme 1 [31]. PCHDs (pre-polymer for PPH) with different 1,2-CHD/1,4-CHD unit ratios were prepared by (living) anionic polymerization of 1,3-CHD with several different initiators (Table 1). The polymer yield (i.e. the conversion from 1,3-CHD to PCHD) for each sample was almost the quantitative yield (>99 wt%). The 1,2-CHD/1,4-CHD unit molar ratios were estimated by ^{1}H NMR [22,31]. Subsequently, dehydrogenation of PCHD-1 to -4 was conducted with DDQ for 96 h (PCHD-1 and -2) or for 168 h (PCHD-3 and -4) at 90 °C under a dry argon atmosphere. The conversion from CHD units to Ph units was 100% and a quantitative yield of completely dehydrogenated PCHD (i.e. soluble PPH homopolymer) was obtained for each sample as an amorphous polymer. The PPH homopolymers were stable in air at room temperature. The results obtained are summarized in Table 1.

This dehydrogenation reaction is an aromatization, therefore, the extent of dehydrogenation of PCHD (the conversion of 1,2-CHD and/or 1,4-CHD units to 1,2-Ph and/or 1,4-Ph units) can be estimated by a decrease in the olefinic signals (Ho at ca. 5.7 ppm, 2H per CHD unit) and an increase in the aromatic signals for the Ph units (Hp at ca. 7.5 ppm, 4H per Ph unit), as measured by ^{1}H NMR [22,31]. Thus, the conversion of 1,2-CHD and/or 1,4-CHD units to 1,2-Ph and/or 1,4-Ph units (z%) were determined using the following formula, where O is the peak area of olefinic signals (Ho) and P is the peak area of aromatic signals for the Ph units (Hp):

$$\frac{z}{100}=\frac{(P/4)}{(O/2+P/4)}=\frac{1}{(1+2O/P)}$$

Typical ^{1}H NMR spectra of a soluble PPH homopolymer (PPH-2) and its pre-polymer (PCHD-2) are presented in Fig. 1.

3.2. Optical properties of soluble polyphenylene homopolymers

UV/vis and PL spectra of PPH homopolymers are shown in Fig. 2. PPH-1 to -4 showed two types of UV/vis spectra, as shown in Fig. 2(a). PPH-1 and -2 exhibited similar UV/vis spectra (Type A), and PPH-3 and -4 showed similar UV/vis spectra (Type B). However, there is a remarkable difference between Type A and Type B spectra [31].

The Type A spectrum shows an absorption band in the region from 260 to 400 nm, and the maximum point (λ_{max}^{ab}) of each absorption was at approximately 330 nm. On the other hand, the Type B spectrum shows two inflection points at approximately 280 nm and 350 nm. The absorption at 330 nm in the Type A spectrum was stronger than that in the Type B spectrum. Thus, the absorption in the region from 310 to 380 nm can be considered to be caused by the 1,4-Ph unit in the polymer chain of the PPH homopolymer, which corresponds to the π–π* transition of the main chain (Fig. 2(a)). In addition, the intensity of the absorption seems to depend on the amount and length of the 1,4-Ph unit sequences. That is, a strong absorption results from long sequences of 1,4-Ph

Table 1
List of evaluated polymers

Soluble polyphenylene homopolymer[a]				Pre-polymer[b]	
Polymer no.	M_n[c]	M_w/M_n[c]	1,2-/1,4-Ph unit (%)[d]	Pre-polymer no.	Initiator system
PPH-1	1380	1.39	2/98	PCHD-1	*s*-BuLi
PPH-2	1700	1.26	6/94	PCHD-2	*s*-BuLi/DABCO (4/5)
PPH-3	1750	1.29	28/72	PCHD-3	*n*-BuLi/TMEDA (4/0.5)
PPH-4	1690	1.23	52/48	PCHD-4	*n*-BuLi/TMEDA (4/5)

[a] Dehydrogenation was carried out in 1,2-dichlorobenzene (20 mL) at 90 °C for 96 h (PPH-1 and -2) and 168 h (PPH-3 and -4). [Polymer]/[solvent] = 0.2 g/20 mL. Conversion from CHD units to Ph units was 100% for each sample.

[b] Polymerization was carried out in cyclohexane (20 mL) for 2.0 h (PCHD-1), 1.0 h (PCHD-2 to -4) [1,3-CHD]/[solvent] = 10/90. $[1,3\text{-CHD}]_0/[\text{Li}]_0 = 12.5$ (PCHD-1), 20.0 (PCHD-2 to -4).

[c] Estimated by GPC, using polystyrene as standard. [Polymer]/[THF] = 0.005 g/5.0 mL.

[d] Estimated from ^{1}H NMR spectra of pre-polymers.

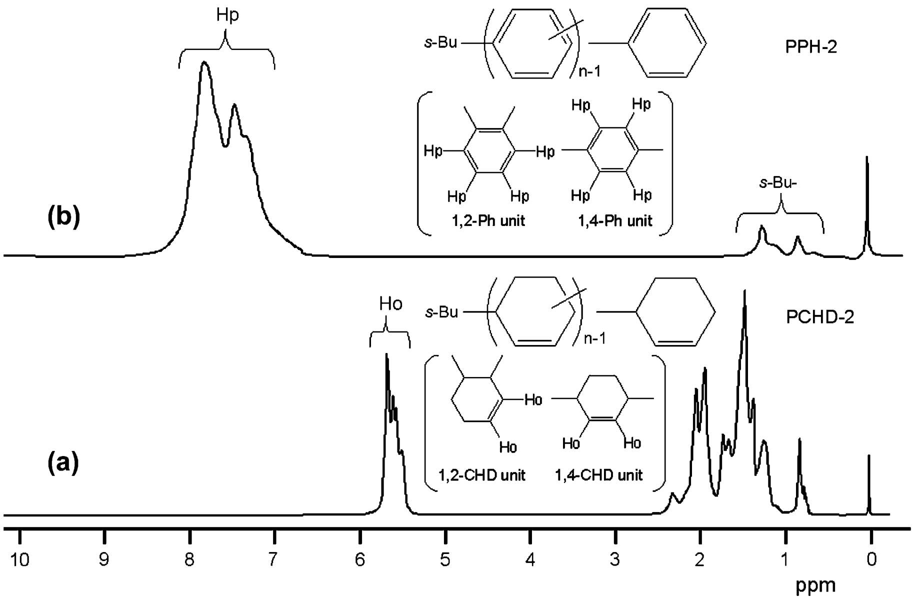


Fig. 1. ^{1}H NMR spectra of the pre-polymer (PCHD) and the completely dehydrogenated polymer (soluble polyphenylene homopolymer): (a) PCHD-2 (1,2-CHD/1,4-CHD units = 6/94) in a 3.0 wt% solution of $CDCl_3$ at 50 °C, (b) PPH-2 (1,2-Ph/1,4-Ph units = 6/94) in a 3.0 wt% solution of DMF-d_7 at 50 °C.

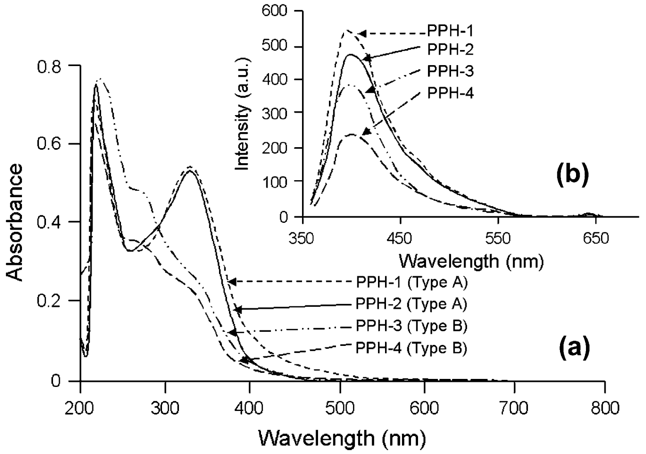


Fig. 2. UV/vis and photoluminescence (PL) spectra of soluble polyphenylene homopolymers: (a) UV/vis spectra of PPH-1 to -4. [Polymer]/[THF] = 0.1 mg/10 mL. (b) PL spectra of PPH-1 to -4. [Polymer]/[THF] = 0.1 mg/10 mL. Excitation wavelength is 330 nm.

units. A weak absorption is caused by small amounts of short 1,4-Ph unit sequences (Table 1).

The band gap energies determined from the UV/vis spectra of PPH-1 to -4 are 3.16, 3.24, 3.18, and 3.23 eV, respectively. Therefore, the molar ratios of 1,2-/1,4-Ph units do not significantly affect the band gap energies of PPH homopolymer, however, the 1,4-Ph unit sequences seem to be the dominating factor that determines the band gap energy for a polymer chain.

The PL analysis was performed for PPH-1 to -4 at an excitation wavelength of 330 nm. The PL spectra obtained are provided in Fig. 2(b). The emission maximum ($\lambda_{\max}^{\mathrm{em}}$) for each spectrum was observed in the region from 390 to 410 nm, and the small fluorescence emission signal at approximately 650 nm seemed to be an intra-molecular excimer-forming fluorescence of PPH homopolymer. The absorbance at the excitation wavelength was decreased with the increasing 1,2-Ph units (Fig. 2(a)), for that reason, the $\lambda_{\max}^{\mathrm{em}}$ of the PL spectra seemed to decrease with the increasing 1,2-Ph units in the polymer chain. Therefore, each PPH homopolymer has PL properties, and the resultant PL spectra correspond to the emission caused by 1,4-Ph units in the polymer chain. In general, the molar ratio of the 1,2-Ph/1,4-Ph units is reflected in the emission intensity of the PL spectra [31].

3.3. Electrochemical properties of soluble polyphenylene homopolymers

In order to reveal the influence of the microstructure on the electrochemical properties of soluble PPH homopolymers, cyclic voltammetry (CV) was performed on thin films of polymer (PPH-1 to -4). This enabled an investigation of the redox behavior of PPH homopolymer and assessment of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels [32,34].

The peaks were referenced to Ag/AgCl and the reduction peak of ferrocene/ferrocenium (FOC). As shown in the anodic and cathodic scans of Fig. 3, each PPH homopolymer shows quasi-reversible *p*- and *n*-doping processes. The anodic scan of the cyclic voltammograms for PPH-1 and -2 each shows one oxidation peak at 0.71 and 0.79 V (vs. Ag/AgCl), respectively (Fig. 3(a) and (b)). On the other hand, the cyclic voltammograms for PPH-3 and -4 each show two oxidation peaks at 0.82/2.07 and 0.71/2.00 V (vs. Ag/AgCl), respectively (Fig. 3(c) and (d)). Therefore, the first oxidation peak of PPH-1 to -4 (from 0.71 to 0.82 V) can be attributed to the oxidation of 1,4-Ph units in the polymer chain, and the second oxidation peak of PPH-3 and -4 (from 2.00 to 2.21) is attributed to the oxidation of 1,2-Ph units in the polymer chain. For the cathodic

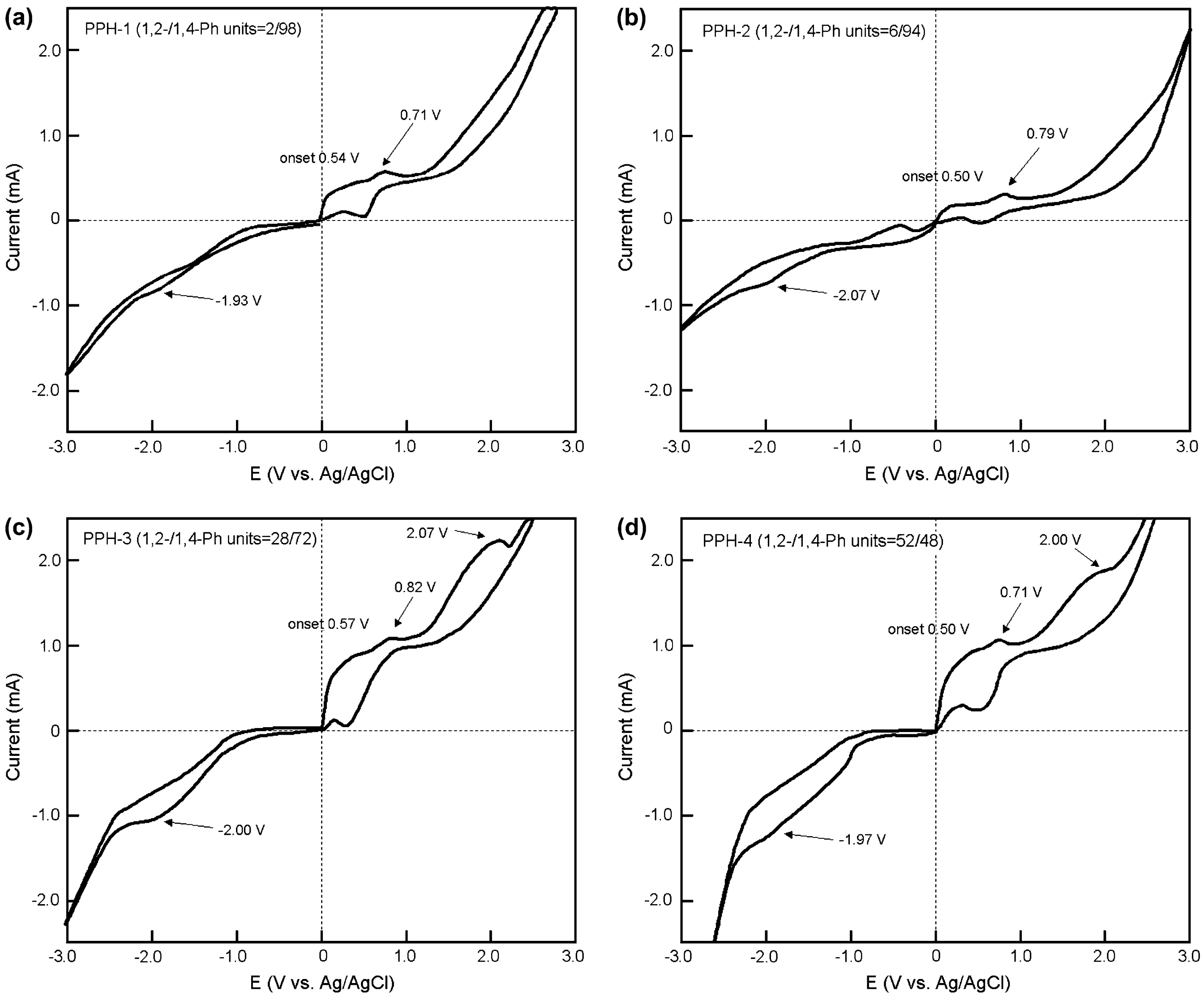


Fig. 3. Cyclic voltammograms of soluble polyphenylene homopolymer thin films (1.0 mm) on Pt disk electrodes (1.6 mm in diameter) in dry acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as an electrolyte. Scan rate = 50 mV/s: (a) PPH-1 (1,2-Ph/1,4-Ph units = 2/98), (b) PPH-2 (1,2-Ph/1,4-Ph units = 6/94), (c) PPH-3 (1,2-Ph/1,4-Ph units = 28/72), (d) PPH-4 (1,2-Ph/1,4-Ph units = 52/48).

scan, the cyclic voltammograms of PPH-1 to -4 each show one reduction peak at approximately −2.0 V (vs. Ag/AgCl), which seems to be attributable to the reduction of 1,2- and 1,4-Ph units in the polymer chain (Fig. 3(a)–(d)). The large background current for each cyclic voltammogram seems to be due to the oxidation and reduction of CH_3CN. The reduction peak of FOC (CH_3CN solution containing 0.1 mM FOC and 0.1 M Bu_4NClO_4) in the cathodic scan CV measurement was at 0.14 V (vs. Ag/AgCl) in this study.

The HOMO energy levels of PPH homopolymers were calculated from the onset of the oxidation peak, assuming that the absolute energy level of FOC is 4.8 eV below the vacuum level [32,33]. The LUMO energy level was calculated from the HOMO energy level and the absorption edge of UV/vis spectra for each PPH homopolymer. The results are summarized in Table 2. The HOMO and LUMO energy levels of PPH-1 to -4 obtained from CV and UV/vis spectra are approximately −5.2 and −2.0 eV, respectively. Therefore, it is clear that the molar ratios of 1,2-/1,4-Ph units in the polymer chain do not significantly affect the HOMO/LUMO energy levels of the PPH homopolymer, as for the band gap energies.

Table 2
Energy levels of soluble polyphenylene homopolymers

Polymer no.	1,2-/1,4-Ph unit (%)[a]	Optical band gap (eV)[b]	HOMO (eV vs. vacuum)[c]	LUMO (eV vs. vacuum)[d]
PPH-1	2/98	3.16	−5.20	−2.04
PPH-2	6/94	3.24	−5.17	−1.93
PPH-3	28/72	3.18	−5.23	−2.05
PPH-4	52/48	3.23	−5.16	−1.93

[a] Estimated from ^{1}H NMR spectra of pre-polymers.

[b] Estimated from the absorption edge of UV/vis spectra.

[c] The reduction peak of FOC was 0.14 V (vs. Ag/AgCl). The HOMO energy level was calculated from the onset of oxidation peak by assuming that the absolute energy level of FOC is 4.8 eV below the vacuum level.

[d] The LUMO energy level was calculated from the HOMO energy level and the absorption edge of UV/vis spectra.

3.4. Influence of the microstructure on drift mobility

In order to determine the drift mobility of soluble PPH homopolymers, DMF solutions of PPH-2 to -4 (polymer/DMF = 0.03 g/1.0 g) [35] were cast on indium tin oxide (ITO) glass (sheet resistance, 30 Ω) by the bar coating method and the polymer films obtained were dried under reduced pressure at room temperature for 24 h. The polymer film thickness was determined to be approximately 1.0 μm. An aluminum (Al) electrode (200 nm thickness) was formed on top of the polymer film using the vacuum deposition method. The drift mobility of PPH-2 to -4 was determined using the TOF method, and the mobility, μ, was calculated according to the following equation:

$$\mu = \frac{L^2}{t_T V},$$

where L is the polymer film thickness, t_T is the transit time, and V is the applied voltage.

For PPH-2 to -4, the generation of carriers (both electron and hole) in the polymer films was observed by flashing a xenon lamp. Thus, these PPH homopolymers appeared to have photocurrent generation properties. The typical TOF transient photocurrent for the electrons in the soluble PPH homopolymer film is shown in Fig. 4 (PPH-3: 1,2-Ph/1,4-Ph units = 28/72) and the shape of the curve indicates the non-dispersive nature of electron transport.

The logarithm of the electron drift mobility for PPH-2 to -4 was plotted against the square root of the applied field [$E^{1/2}$(V/cm)$^{1/2}$], as shown in Fig. 5. It was observed that the microstructure of the PPH homopolymer strongly affects the electron drift mobility. The electron drift mobility for PPH-2 (1,2-/1,4-Ph units = 6/94) was in the order of 10^{-4} to 10^{-5} (cm^2/Vs) with a negative slope. A decrease in the electron drift mobility was observed with an increase of 1,2-Ph units in the polymer chain (Fig. 5). The electron drift mobility for PPH-3 and -4 was in the order of 10^{-5} (cm^2/Vs) with almost zero gradients. Therefore, 1,2-Ph units seem to determine the electron drift mobility in the polymer chain of PPH homopolymers.

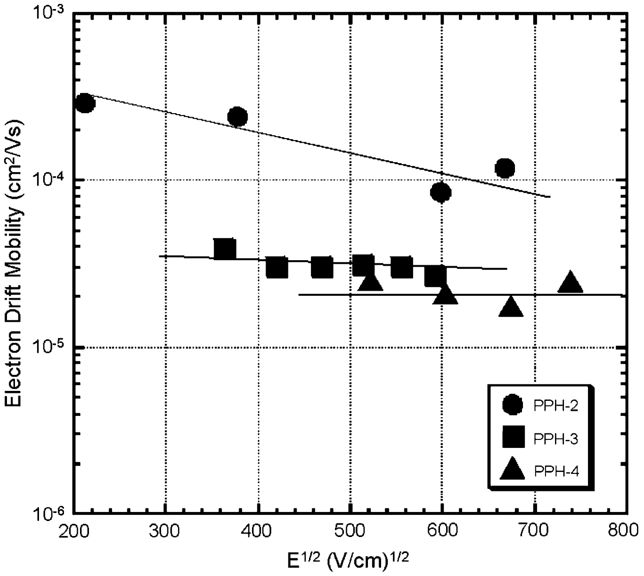


Fig. 5. Electron drift mobility dependence on applied field for thin films of soluble polyphenylene homopolymers (PPH-2 to -4).

Fig. 6 shows the hole drift mobility for PPH-2 to -4 plotted against the square root of the applied field [$E^{1/2}$(V/cm)$^{1/2}$]. The hole drift mobility for PPH-2 to -4 was not so different to the electron drift mobility. Although the hole drift mobility for PPH-2 was somewhat faster than that for PPH-3 (1,2-/1,4-Ph units = 28/72) and PPH-4 (1,2-/1,4-Ph units = 52/48), each PPH homopolymer showed the same order of 10^{-5} (cm^2/Vs) for hole drift mobility with almost zero gradients. The influence of the 1,2-/1,4-Ph unit molar ratios on the hole drift

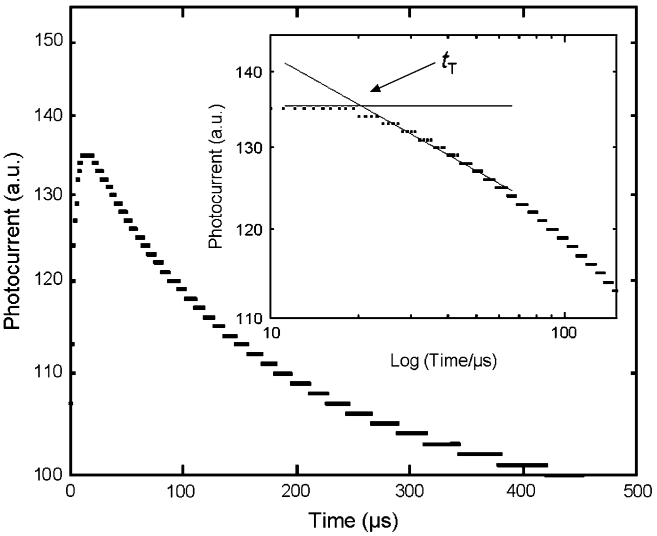


Fig. 4. Typical transient photocurrent profiles due to the electron transport in ITO glass/PPH-3 (1,2-Ph/1,4-Ph units = 28/72)/Al cell at 3.1 × 10^5 V/cm and at room temperature (ca. 25 °C).

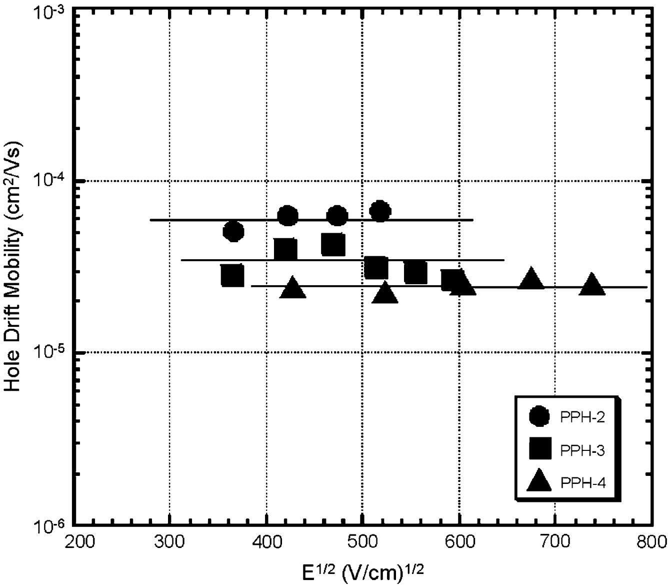


Fig. 6. Hole drift mobility dependence on applied field for thin films of soluble polyphenylene homopolymers (PPH-2 to -4).

mobility does not seem to be so strong for PPH homopolymers. Furthermore, the drift mobility of electrons and holes was almost the same for PPH-3 and -4.

Therefore, the intra-molecular transfer rate seems to be a major factor for the electron drift mobility of PPH homopolymers. On the other hand, the inter-molecular transfer rate seems to be important for the hole drift mobility of PPH homopolymers.

3.5. Current–voltage (I–V) characteristics of soluble polyphenylene homopolymers

In order to know the influence of microstructure on the *I*–*V* characteristics of soluble PPH homopolymers, DMF solutions of PPH-2 and -4 (polymer/DMF = 0.03 g/1.0 g) were spin-coated onto ITO glass (sheet resistance, 30 Ω), and the polymer films obtained were dried under reduced pressure at room temperature for 24 h. The film thickness was determined to be approximately 150 nm. Subsequently, aluminum (Al) was evaporated onto the polymer layer as a cathode (100 nm thickness). The *I*–*V* characteristics were then measured for each polymer film of PPH-2 and -4. Typical *I*–*V* curves are given in Fig. 7.

The current in PPH-2 and -4 increased with forward bias voltage applied showing the rectification properties. This is the typical Shottky diode behavior attributable to the fact that ITO forms an ohmic contact while Al forms a blocking contact. In addition, the current density of PPH-2 at 4 V was considerably higher than that of PPH-4. Therefore, the *I*–*V* characteristics of soluble PPH homopolymers are thought to be controllable by the microstructure of PPH.

4. Conclusion

The optical and electrical characteristics of soluble PPH homopolymers obtained by the complete dehydrogenation of PCHD were reported for the first time. The optical properties (e.g. UV/vis and PL spectra) were strongly affected by the molar ratios of 1,2-/1,4-Ph units. The HOMO and LUMO energy levels of PPH homopolymers were approximately −5.2 and −2.0 eV, respectively. The microstructure did not significantly influence the HOMO and LUMO energy levels or the band gap energies. The generation of carriers (electron and hole) was observed in the polymer films, and the electron and hole drift mobilities were affected by the molar ratios of 1,2-/1,4-Ph units in the polymer chain. The electron drift mobility for PPH homopolymers with a high content of 1,4-Ph units was in the order of 10^{-4} to 10^{-5} (cm^2/Vs). The *I*–*V* characteristics of soluble PPH homopolymers were controllable by the microstructure of PPH. The 1,2-Ph unit is not considered to be a defect in the polymer chain, and the 1,2-Ph unit imparts appropriate solubility and toughness to PPH homopolymers. These results obtained concerning soluble PPH homopolymers should accelerate the development of new π-conjugated polymer semiconductors containing six-membered hydrocarbon rings as a key molecular structure.

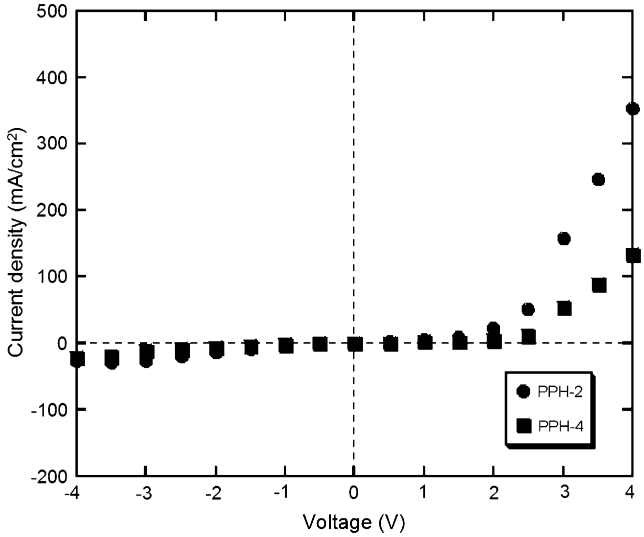


Fig. 7. Current–voltage (*I*–*V*) characteristics of soluble polyphenylene homopolymer (PPH-2: 1,2-Ph/1,4-Ph units = 6/94, PPH-4: 1,2-Ph/1,4-Ph units = 52/48) films on ITO glass.

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