

ORIGINAL ARTICLE

Synthesis and properties of conjugated polymers from 3,6-di(4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester and application to the photo-sensitizer of a solar cell

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Ni(0)-catalyzed coupling polymerizations of 3,6-di(4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester **1** were accompanied by isomerization of the 1,4-cyclohexadiene moiety into a 3,5-cyclohexadiene group, yielding a conjugated polymer. The structure of this conjugated polymer was the same as that of the conjugated polymer from 3,6-di(4-chlorophenyl)-1,2-dihydrophthalic acid diethyl ester **2**. The number-average degree of polymerization was only ~ 7 due to the low solubility of the conjugated polymer. The conjugated polymer exhibited a λ max at 430 nm in the absorption spectrum, and could be applied as a photo-sensitizer of a solar cell. The incident monochromatic photon (450 nm)-to-current conversion efficiencies of photocurrent from an indium-titanium oxide (ITO)/TiO₂ electrode modified with the conjugated polymer was 6.1% in the I₃⁻-3I⁻ electrolyte wet system. The conjugated polymer exhibited a glass transition temperature of 210 °C and was converted by thermal treatment at 300 °C to poly(*p*-phenylene) (PPP) with the elimination of ethoxycarbonyl groups. *Polymer Journal* (2013) **45**, 790–796; doi:10.1038/pj.2012.228; published online 30 January 2013

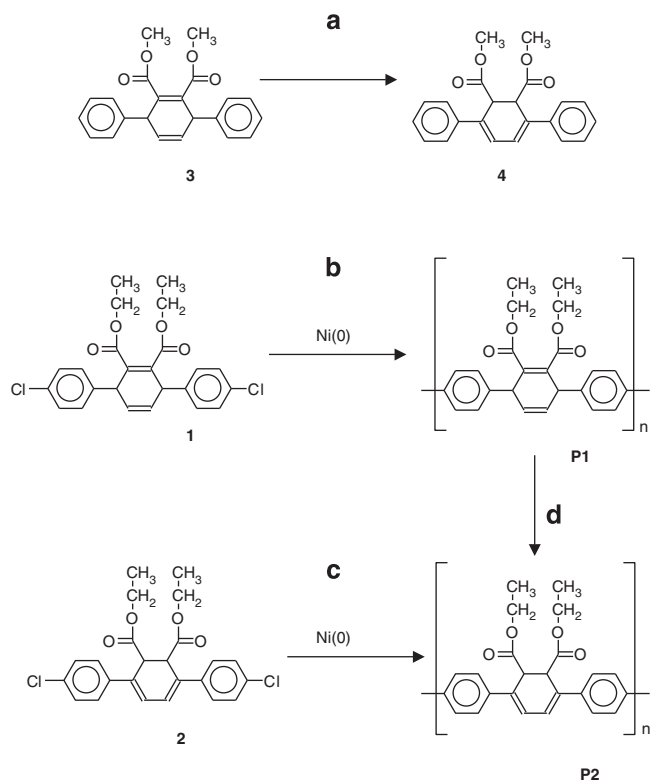
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INTRODUCTION

Conjugated polymers are of great inherent interest for the development of optical and electronic applications because of the extended π -electron delocalization along their backbone. However, a problem in the synthesis of conjugated polymers is their insolubility due to their rigid backbones. For example, direct polymerization of benzene using electrochemical or chemical oxidation techniques only produces oligomers as a result of the inherent insolubility of the growing polyphenylene chains (these chains have number-average degrees of polymerization (DP) of 15–20).¹ Soluble π -conjugated polymers with alkyl or alkyloxy substituents were synthesized,^{2–4} with representative examples being poly([2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene])⁵ and poly(3-hexylthiophene).^{6–7} Higher molecular weight conjugated polymers without substituents were obtained by an indirect method that involved the synthesis of a soluble non-conjugated precursor followed by its chemical transformation into a conjugated polymer. Additionally, poly(*p*-phenylene)s were synthesized via 1,3-cyclohexadiene derivative routes,^{8–13} and poly(phenylenevinylene)s and poly(thienylene vinylene)s were synthesized via the Gilch,¹⁴ Wessling–Zimmerman

precursor,^{15–16} the xanthate precursor¹⁷ and the sulphinyl precursor routes.^{18–20} The elimination of low molecular weight compounds, such as hydrogen, halogens, acetic acid and dithiocarbamate, accompanied all of the conversions of precursor non-conjugated polymers to conjugated polymers. 3,6-diphenyl-3,6-dihydrophthalic acid dimethyl ester **3**, a non-conjugated compound, was converted to 3,6-diphenyl-1,2-dihydrophthalic acid dimethyl ester **4**, a conjugated compound (Scheme 1a).²¹

In this study, we examined the preparation of a conjugated polymer by a two-step procedure involving the synthesis of a non-conjugated polymer and its subsequent conversion to a conjugated polymer. The synthesis of **P1** by Ni(0)-catalyzed coupling polymerizations^{22–26} of 3,6-di(4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester **1** (Scheme 1b) and the conversion of the non-conjugated polymer **P1** to the conjugated polymer **P2** (Scheme 1d) were examined. **P2** was directly synthesized from **2** for comparison (Scheme 1c). As the elimination of low molecular weight compounds does not accompany the conversion of **P1** to **P2**, this conversion is expected to proceed under mild conditions. The conjugated polymer **P2** was characterized by ¹H NMR (nuclear magnetic resonance), absorption spectroscopy,



Scheme 1 (a) Isomerization of **3** into **4**. (b) Ni(0)-catalyzed polymerization of **1**. (c) Ni(0)-catalyzed polymerization of **2**. (d) Isomerization of non-conjugated polymer into conjugated polymer.

differential scanning calorimetry (DSC) and thermogravimetry (TG), and investigated for applications as a photo-sensitizer of solar cells.²⁷ As *p*-terphenyls have been reported to be easily prepared by oxidative decarboxylation of 3,6-diphenyl-1,2 dihydrophthalic acid derived from **4**,²¹ the conversion of **P2** to poly(*p*-phenylene) was also investigated.

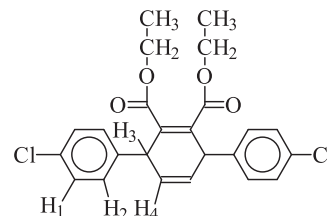
EXPERIMENTAL PROCEDURE

Materials

NiCl₂(PPh₃)₂ (Cotton *et al.*²⁴) was purchased from Aldrich (Milwaukee, WI, USA). NiBr₂, NiCl₂, triphenylphosphine, Et₄Ni, 4-chlorobenzaldehyde, acetaldehyde, 4-chlorobenzylchloride, acetylenedicarboxylate, sodium and phenol were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. Toluene and dioxane were freshly distilled over sodium benzophenone ketyl under a nitrogen atmosphere before use. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and freshly distilled over calcium hydride. NaCl, acetonitrile, tetrapropylammonium iodide, KI and I₂ were purchased from Wako Pure Chemical Industries and used as received.

3,6-Di (4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester (1)

A solution of (*E,E*)-1,4-bis(4-chlorophenyl)-1,3-butadiene (5.50 g, 0.02 mol) and diethyl acetylenedicarboxylate (10.2 g, 0.06 mol) in phenol (30 ml) was heated at reflux temperature for 1 h. After the reaction mixture was cooled to 80 °C, the phenol was evaporated under reduced pressure of 15–20 torr. Pure **1** was obtained by recrystallization from ethanol. The yield was 5.79 g (65%), while the Mp was 96–98 °C. The infrared (IR) spectrum exhibited absorption bands at 2980 cm⁻¹, 2930 cm⁻¹ (–C₂H₅), 1720 cm⁻¹ (C=O), 1615 cm⁻¹ and 1600 cm⁻¹ (C=C).

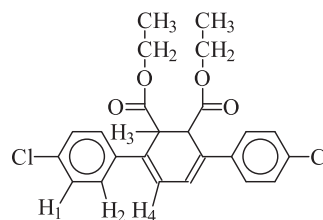


The ¹H NMR spectrum [δ in DMSO-*d*₆] showed signals at 0.98 (t, 6H, *J* = 7.0 Hz, CH₃-), 3.97 (d, 2H, *J* = 7.0 Hz, –CH₂-), 3.98 (d, 2H, *J* = 7.0 Hz, –CH₂-), 4.53 (s, 2H, H₃), 5.76 (s, 2H, H₄), 7.24 (d, 4H, *J* = 8.8 Hz, H₁) and 7.44 (d, 4H, *J* = 8.8 Hz, H₂). The ¹³C NMR spectrum [δ in DMSO-*d*₆] showed signals at 13.44, 42.21, 60.59, 125.74, 128.53, 129.83, 131.51, 134.91, 140.08 and 166.18 p.p.m.

Analysis calculated for C₂₄H₂₂Cl₂O₄: C, 64.73%; H, 4.98%. Found: C, 64.55%; H, 4.87%.

3,6-Di (4-chlorophenyl)-trans-1,2-dihydrophthalic acid diethyl ester (2)

1 (4.45 g, 0.01 mol) was added to a solution of KOH (1.00 g, 0.017 mol) in methanol (20 ml), and stirred at 50 °C for 20 min. The reaction mixture was cooled to room temperature, and poured into water (300 ml). The precipitate was collected by filtration, and the pure **2** was obtained by recrystallization from methanol. The yield was 3.92 g (88%), while the Mp was 111–113 °C. The IR spectrum exhibited absorption bands at 2980 cm⁻¹, 2930 cm⁻¹ (–C₂H₅), 1725 cm⁻¹ (C=O) and 1610 cm⁻¹ (C=C).

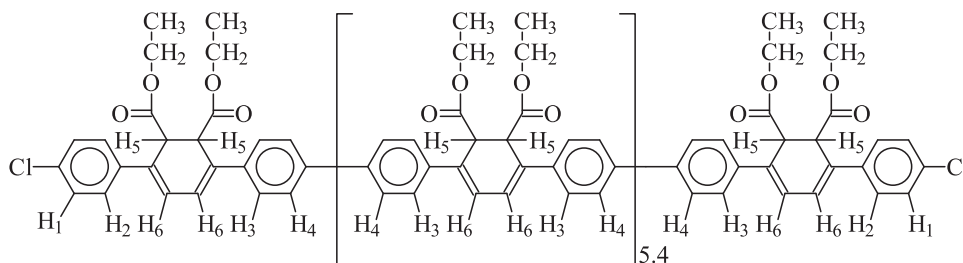


The ¹H NMR spectrum [δ in DMSO-*d*₆] showed signals at 1.00 (t, 6H, *J* = 7.0 Hz, CH₃-), 3.97 (d, 2H, *J* = 7.0 Hz, –CH₂-), 3.98 (d, 2H, *J* = 7.0 Hz, –CH₂-), 4.54 (s, 2H, H₃), 6.57 (s, 2H, H₄), 7.29 (d, 4H, *J* = 8.8 Hz, H₁) and 7.45 (d, 4H, *J* = 8.8 Hz, H₂). The ¹³C NMR spectrum [δ in DMSO-*d*₆] showed signals at 13.45, 42.23, 66.38, 125.76, 128.53, 129.82, 131.53, 134.92, 140.08 and 166.21 p.p.m.

Analysis calculated for C₂₄H₂₂Cl₂O₄: C, 64.73%; H, 4.98%. Found: C, 64.60%; H, 4.85%.

Ni(0)-catalyzed polymerization of 1

A 50-ml three-necked flask equipped with a condenser tube was charged with nickel(II) bromide (55 mg, 0.25 mmol), triphenylphosphine (0.50 g, 1.9 mmol), zinc powder (0.505 g, 7.72 mmol) and a magnetic stir bar. The flask was sealed with a rubber septum and placed under a dry N₂ atmosphere. Freshly distilled DMF (20 ml) was added via a syringe through the rubber septum, and the mixture was stirred at 60 °C for 10 min. After the mixture had turned red-brown, **1** (0.94 g, 2.1 mmol) was added as a solid and the polymerization was performed at 80 °C for 48 h. After ~16 h, the reaction solution became yellow, followed by the precipitation of the generated yellow polymer. The reaction mixture was cooled to room temperature, and poured into acetone (250 ml). The precipitate was collected by filtration, and washed thoroughly with 2 M HCl and hot hexane. The IR spectrum exhibited absorption bands at 2980 cm⁻¹, 2930 cm⁻¹ (–C₂H₅), 1720 cm⁻¹ (C=O), 1600 cm⁻¹ (C=C) and 1470 cm⁻¹ (aromatic ring).

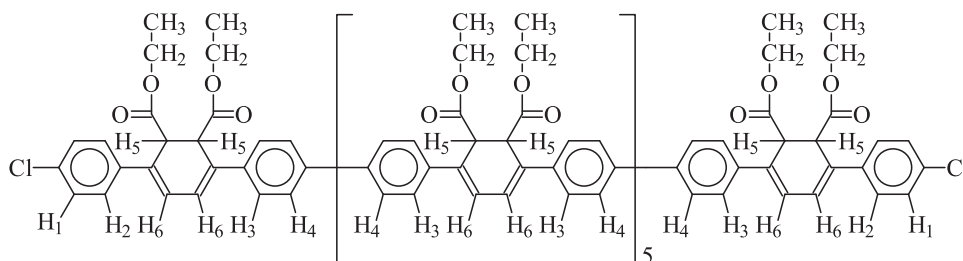


The ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 0.90–1.33 (6H, CH_3 -), 3.90–4.20 (4H, $-\text{CH}_2$ -), 4.53–4.70 (2H, H5), 6.74–6.92 (2H, H6), 7.24–7.48 (1.08H, H1 + H2) and 7.50–7.90 (6.92H, H3 + H4).

Analysis calculated for $\text{C}_{177.6}\text{H}_{162.8}\text{Cl}_2\text{O}_{29.6}$: C, 75.07%; H, 5.77%. Found: C, 74.75%; H, 5.69%.

Ni(0)-catalyzed polymerization of 2

A 50-ml three-necked flask equipped with a condenser tube was charged with $\text{NiCl}_2(\text{PPh}_3)_2$ (0.16 g, 0.25 mmol), triphenylphosphine (0.39 g, 1.5 mmol), zinc powder (1.01 g, 15.4 mmol), Et_4Ni (0.96 g, 3.75 mmol) and a magnetic stir bar. The flask was sealed with a rubber septum and placed under a dry N_2 atmosphere. Freshly distilled DMF (20 ml) was added via syringe through the rubber septum, and the mixture was stirred at 60°C for 10 min. After the mixture had turned red-brown, **2** (0.94 g, 2.1 mmol) was added as a solid and the polymerization was performed at 80°C for 48 h. After ~ 16 h, the reaction solution became yellow, followed by the precipitation of the generated yellow polymer. The reaction mixture was cooled to room temperature, and poured into acetone (250 ml). The precipitate was collected by filtration, and washed thoroughly with 2 M HCl and hot hexane. The IR spectrum exhibited absorption bands at 2980 cm^{-1} , 2930 cm^{-1} ($-\text{C}_2\text{H}_5$), 1720 cm^{-1} (C=O), 1600 cm^{-1} (C=C) and 1470 cm^{-1} (aromatic ring).



The ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 0.90–1.33 (6H, CH_3 -), 3.90–4.20 (4H, $-\text{CH}_2$ -), 4.53–4.70 (2H, H5), 6.74–6.92 (2H, H6), 7.24–7.48 (1.14H, H1 + H2) and 7.50–7.90 (6.86H, H3 + H4).

Analysis calculated for $\text{C}_{166}\text{H}_{154}\text{Cl}_2\text{O}_{28}$: C, 74.95%; H, 5.77%. Found: C, 74.45%; H, 5.53%.

Measurements

^1H and ^{13}C NMR spectra were recorded on a JNM-GSX400 FT-NMR spectrometer (JEOL, Tokyo, Japan), and IR spectra were recorded on a Shimadzu spectro-photometer IR 435 (Shimadzu Corporation, Kyoto, Japan). A Shimadzu DSC-60 (Shimadzu Corporation) and Rigaku thermal analysis station TG 8110 (Rigaku Corporation, Tokyo, Japan) were used for DSC and TG, respectively, and measurements were made at a heating rate of $10^\circ\text{C min}^{-1}$ in air or nitrogen.

The photoelectrochemical properties were measured as follows. A colloidal aqueous solution of TiO_2 , sample P-25 (Japan Aerosil Co. Ltd, Tokyo, Japan), was spin-coated on an indium-titanium oxide (ITO) electrode (Furuuchi Chemical Corporation, Tokyo, Japan) and heated at 100°C for 30 min, and the ITO/ TiO_2

electrode was heated at 450°C for 30 min to prepare a nanoporous TiO_2 thin film of $\sim 5\text{ }\mu\text{m}$ thickness. The TiO_2 -coated ITO was soaked in a diluted NMP solution (0.2 wt%) of the conjugated polymer for 12 h, and the solvent was removed at 80°C to prepare the ITO/ TiO_2 electrode modified with the conjugated polymer. The modified electrode was washed with water to remove NMP completely. The effective area of the modified ITO/ TiO_2 electrode was adjusted to 1.0 cm^2 . The photocurrents were measured using a three-electrode cell consisting of the working electrode, a Pt counter electrode (Hokuto Denko Corporation, Tokyo, Japan) and saturated calomel electrode (Hokuto Denko Corporation) as the reference electrode in an electrolyte solution. Two types of solutions, an aqueous solution containing 0.8 M NaCl and an acetonitrile solution containing 0.5 M tetrapropylammonium iodide, 0.02 M KI and 0.04 M I_2 , were used as the electrolyte solutions.

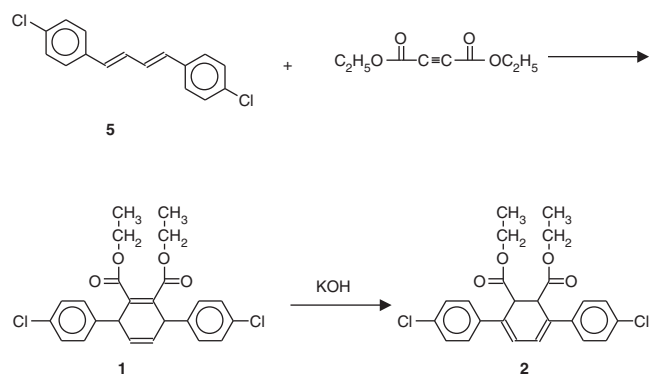
A Hokuto Denko HA-501 M potentiostat (Hokuto Denko Corporation) was employed to study the photoelectrochemical properties. An Ushio Denki 500 W Xe lamp (Ushio Denki Corporation, Tokyo, Japan) was used as the light source, and the Xe lamp light was monochromatized by a Shimadzu SPG-100ST monochromator (Shimadzu Corporation).

RESULTS AND DISCUSSION

Monomer synthesis

3,6-Di(4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester **1** was synthesized by the Diels-Alder reaction of (*E,E*)-1,4-bis(4-chlorophenyl)-1,3-butadiene **5** (Kamigata *et al.*²⁸) according to Scheme 2 with diethyl acetylenedicarboxylate. **5** was synthesized by a similar synthetic method to that of (*E,E*)-1,4-bis(phenyl)-1,3-butadiene,^{21,29–30} which is described in the Supplementary Information. The two 4-chlorophenyl groups are thought to lie on the same side of the 1,4-cyclohexadiene ring according to a crystal structure for 3,6-di(4-bromophenyl)-3,6-dihydrophthalic acid diethyl ester synthesized by the same method.³¹ subsequently, **2** was obtained by treatment of **1** with potassium hydroxide in methanol. The two ester moieties are assumed to have the trans configuration as they do in compound **3**.²¹

Chemical structures were confirmed by IR and NMR spectroscopies and elemental analysis. Compound **1** showed an IR absorption band at 1720 cm^{-1} characteristic of a carbonyl group. The ^{13}C NMR spectrum of **1** exhibited 10 peaks due to symmetry, indicating the formation of the desired structure. The ^{13}C NMR spectrum of **2** also exhibited 10 peaks. Elemental analyses of the compounds were



Scheme 2 Synthesis of **1** and **2**.

also in good agreement with calculated results for the proposed structures.

Ni(0)-catalyzed polymerization

A coupling reaction by Ni(0) catalysts from air stable precursors was used for polymerization of **1** (Scheme 1b). The method involved the generation of the Ni(0) catalyst upon the addition of solvents to a mixture of the Ni(II) compound, triphenylphosphine and Zn under an inert atmosphere. After stirring the mixture for 5 min, the formation of Ni(0) was indicated by a red-brown color. Next, **1** was added, and the reaction mixture was stirred at 80 °C for 48 h. The reaction solution became yellow after ~16 h, followed by the precipitation of the generated yellow polymers. After the reaction mixture was poured into acetone, the resulting precipitate was washed with 2 M HCl and hot hexane to remove Zn and triphenylphosphine, respectively. The solubility of the polymer was very low, dissolving only concentrations of 1 wt% or less, even in hot NMP, DMF, *N,N*-dimethylacetamide and dioxane. For comparison, polymerization of **2** was also performed by the coupling reaction with Ni(0) catalysts. In the polymerizations of **2**, conjugated polymers were directly prepared (Scheme 1c).

The ¹H NMR spectrum of the polymer from **1** was compared with that of the polymer from **2** (Figure 1). ¹H NMR spectra of the starting **1** and **2** are also shown (Figure 1). In the ¹H NMR spectrum of the polymer from **2** (Figure 1b), the resonances attributed to 1,2-protons (H5) and 4,5-protons (H6) of the diethyl 1,2-dihydrophthalate unit are observed at ~4.6 and 6.8 p.p.m., respectively. In the ¹H NMR spectrum (Figure 1d) of the polymer from **1**, the resonances attributed to the 4,5-protons of the diethyl 3,6-dihydrophthalate unit are not observed around 5.8 p.p.m., as in starting **1**; instead, resonances around 6.8 p.p.m. are observed. The ¹H NMR spectrum (Figure 1d) of the polymer from **1** is the same as that (Figure 1b) of the polymer from **2**, and the resonances around 6.8 p.p.m. in the ¹H NMR spectrum of the polymer from **1** are attributed to the 4,5-protons of the diethyl 1,2-dihydrophthalate unit. The conjugated polymer, whose structure is the same as that of the conjugated polymer from **2**, was generated by isomerization of the 1,4-cyclohexadiene moiety into a 3,5-cyclohexadiene moiety during the polymerization of **1**. The isomerization of monomer **3** to monomer **4** is reported to involve abstraction of a hydrogen ion in the benzyl position of **3** by OH⁻ and transfer of the generated carbanion to a stable structure.²¹ Although PPh₃ is a weak base, the polymerization of **1** is thought to be accompanied by abstraction of the benzyl proton due to the electron-withdrawing effect²⁵ by the generated Ni(II).

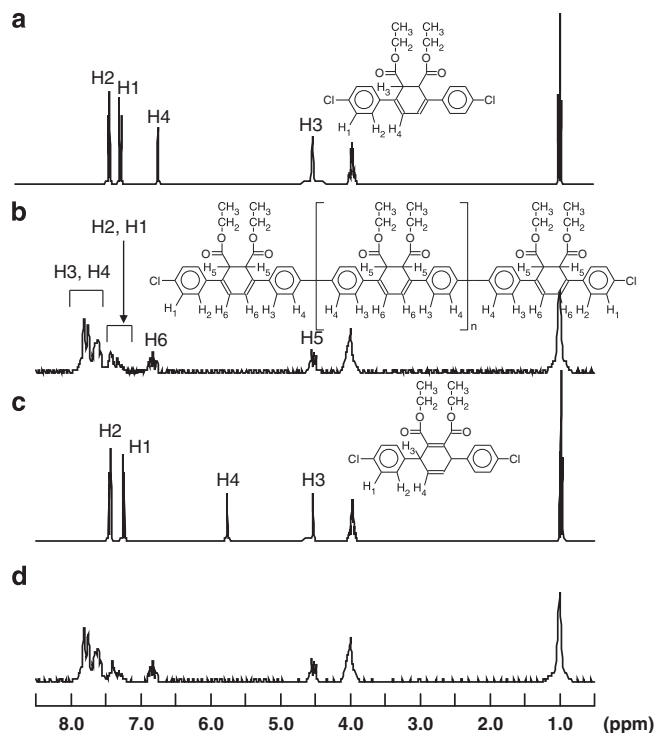


Figure 1 ¹H NMR (nuclear magnetic resonance) spectra. (a) **2**, (b) polymer from **2**, (c) **1**, and (d) polymer from **1**.

Number-average DP = $n + 2$ were determined by the ratio of aromatic protons in the terminus to those in the main chain of the conjugated polymers. In the ¹H NMR spectra (Figure 1b and d) of the conjugated polymers, the resonances at 7.24–7.48 p.p.m. are attributed to protons (H1 and H2) in the terminal chlorophenyl groups, and those at 7.50–7.90 p.p.m. are attributed to protons (H3 and H4) in the phenylene groups in the main chain of the conjugated polymers. The DP values were calculated from integration of the resonances. The polymerizations of **1** and **2** were examined under conditions using NiCl₂(PPh₃)₂ and NiBr₂ as Ni(II) compounds (described in the (Supplementary Information)). The highest DP value of the polymer from **1** was 7.4, while that from **2** was 7.0. Elemental analysis values were in agreement with calculations of the DP values and the chlorines at the end of the conjugated polymers.

Figure 2 shows ultraviolet–vis absorption spectra of the conjugated polymer from **1** in DMF solution. A λ_{max} value is observed at 430 nm, and the molar absorption coefficient is $1.02 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. The spectrum of the conjugated polymer from **2** exhibits the same absorption profile. The polymer is more conjugated than unsubstituted poly(*p*-phenylene) ($\lambda_{\text{max}} = 380 \text{ nm}$).³² The energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the optimized structure of the conjugated polymer with DP = 7 were calculated. Density functional theory calculations were carried out with the Gaussian09W package of quantum chemical programs. The optimized structure of the conjugated polymer was obtained by the RHF/6-31G method in the gas phase. The calculated energy gap between HOMO and LUMO of the conjugated polymer was 3.03 eV, and the λ_{max} calculated from the energy gap value was 410 nm, which was mostly in agreement with that of the absorption spectrum.

Figure 3 shows the optimized structure of the conjugated polymer. The average dihedral angle between the 1,4-phenylene rings was 35.5°,

those between the 1,4-phenylene ring and 3,5-cyclohexadiene were 22.4° and 37.7° , respectively, and that between the double bonds in the 3,5-cyclohexadiene moiety was 16.2° . The average dihedral angle between the 1,4-phenylene rings in $C_6H_5(C_6H_4)_{19}C_6H_5$ was 35.8° . Most of the dihedral angles in the present conjugated polymer were

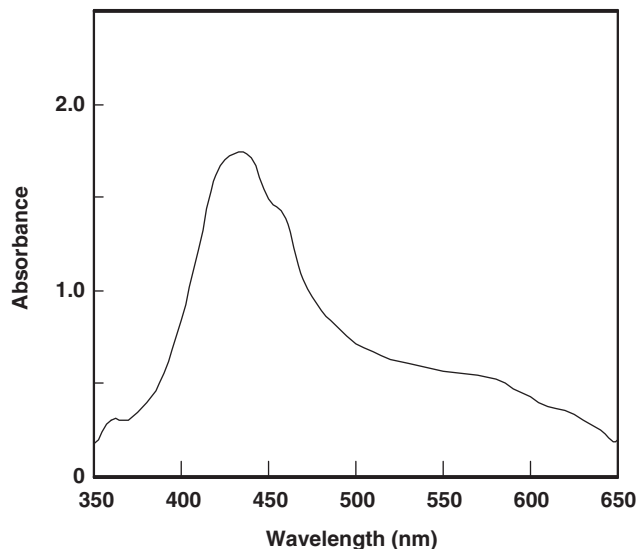


Figure 2 Ultraviolet-vis spectrum of conjugated polymer in *N,N*-dimethylformamide solution at the concentration of 4.9 mg in 10 ml.

lower than those in $C_6H_5(C_6H_4)_{19}C_6H_5$, and the conjugated polymer was suggested to be more planar than poly(*p*-phenylene). The λ_{\max} of monomer 1 and monomer 2 in dichloromethane solution were 270 and 330 nm, respectively.

Application to photo-sensitizer of solar cell

The λ_{\max} is 430 nm in the absorption spectrum of the conjugated polymer, which is close to the λ_{\max} (450 nm) in the energy spectrum of sunlight. Therefore, the conjugated polymer was investigated as a photo-sensitizer of solar cells. The development of polymeric solar cells is accelerating with the needs of new clean energy sources.^{26,33–38}

The ITO/TiO₂ electrode, modified with the conjugated polymer by coating with the diluted NMP solution, was used as the working electrode. The photoelectrochemical properties were measured using a three-electrode cell consisting of the working electrode, a Pt counter electrode, and saturated calomel electrode as the reference electrode in an electrolyte solution. This system works as follows: (1) the conjugated polymer is excited by the irradiation of light, (2) the excited electrons are transferred to the TiO₂ electrode, (3) the missing electrons in the conjugated polymer are supplied from the electrolyte, and (4) the electrolyte accepts electrons at the surface of the counter electrode. Two types of solutions, an aqueous solution containing 0.8 M NaCl and an acetonitrile solution containing 0.5 M tetrapropylammonium iodide, 0.02 M KI and 0.04 M I₂, were used as the electrolyte solutions.

Figure 4 shows the anodic photocurrent action spectra and the absorption spectrum of the conjugated polymer solution. The photocurrent spectra were measured without bias potentials. The fact

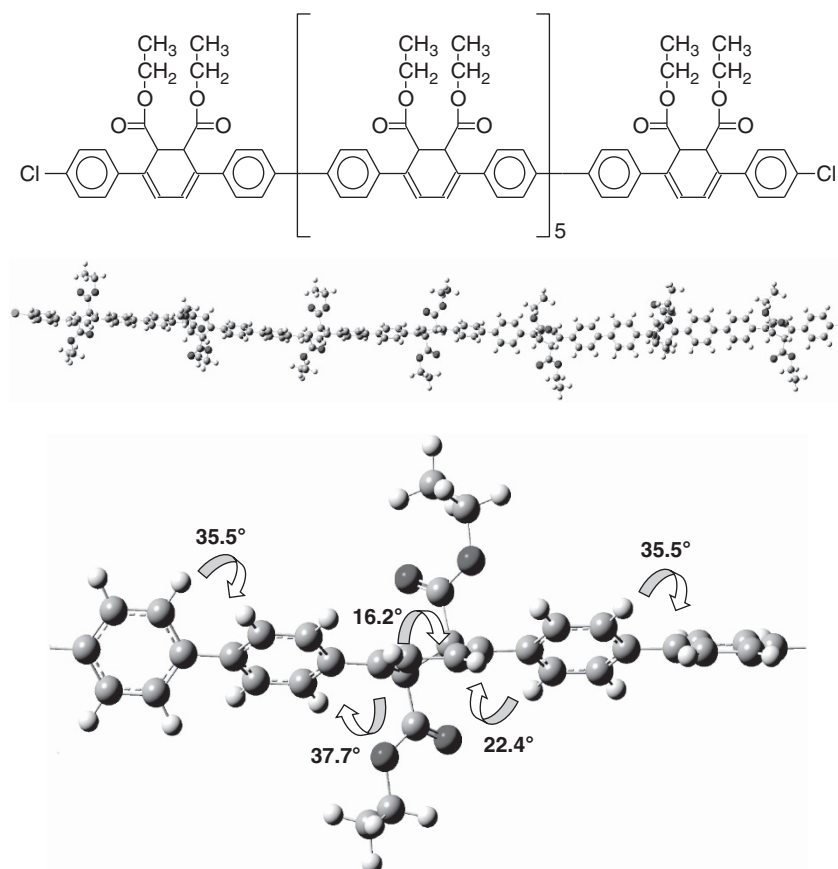


Figure 3 Optimized structure of conjugated polymer with degree of polymerization = 7. A full color version of this figure is available at *Polymer Journal* online.

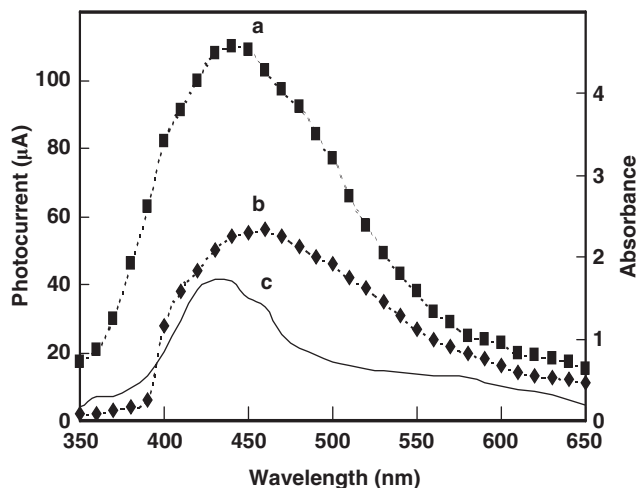


Figure 4 Photocurrent from indium-titanium oxide (ITO)/TiO₂ electrode modified with the conjugated polymer and its absorption spectra. (a) Photocurrent in I₃⁻-3I⁻ electrolyte, (b) photocurrent in NaCl electrolyte, and (c) absorption of a *N,N*-dimethylformamide solution of the polymer.

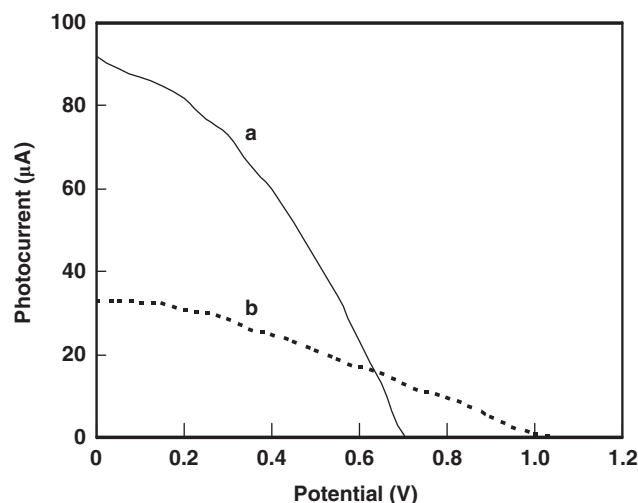


Figure 5 Photocurrent-Voltage characteristics of conjugated polymer solar cell under 450 nm light illumination of 4.9 mW cm⁻². (a) Photocurrent in I₃⁻-3I⁻ electrolyte and (b) photocurrent in NaCl electrolyte.

that the action spectra were very similar in shape to the absorption spectrum implied that the electrons were transferred only from the excited conjugated polymer to the ITO/TiO₂ electrode by the irradiation of light. The slight red-shift of the maximum peak compared with the absorption spectrum in solution may be attributed to aggregation or interaction of the polymer chains. The incident monochromatic photon (450 nm)-to-current conversion efficiencies (IPCE), defined as the number of electrons generated by light in the external circuit divided by the number of incident photons, were 3.1% and 6.1% in the NaCl electrolyte and I₃⁻-3I⁻ electrolyte, respectively. The lower IPCE value in the NaCl electrolyte is thought to be due to the generation of Cl₂ in the electron transfer from Cl⁻ to the electron-deficient conjugated polymer. The anodic photocurrent was not generated from the ITO/TiO₂ electrode without the conjugated polymer.

Figure 5 shows photocurrent-voltage characteristics of the cells under 450 nm light illumination. Open circuit voltage (V_{oc}) and

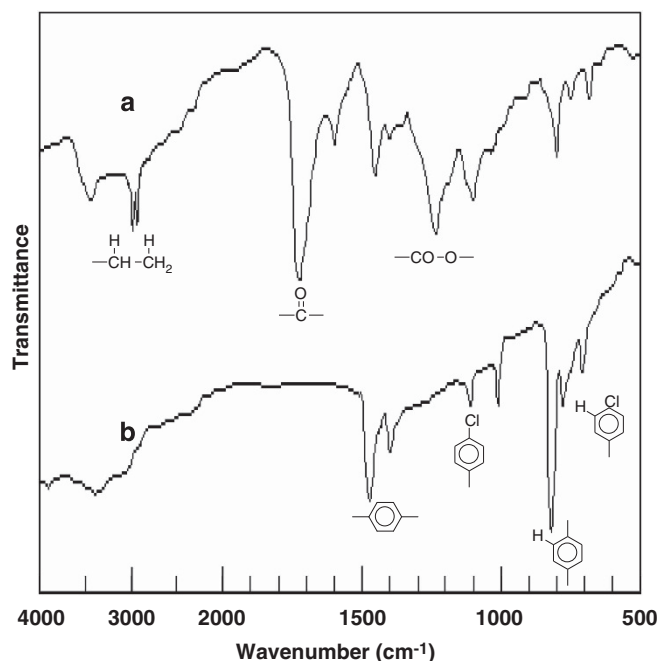


Figure 6 Infrared spectra of (a) conjugated polymer and (b) poly(*p*-phenylene) from thermal conversion of conjugated polymer.

short-circuit photocurrent (i_{sc}) of the cell using the NaCl electrolyte were 1.05 V and 34 μA, respectively, and the energy conversion efficiency (η) was 0.21%. V_{oc} and i_{sc} of the cell using the I₃⁻-3I⁻ electrolyte were 0.70 V and 92 μA, respectively, and η was 0.49%. The difference in the V_{oc} values is due to the oxidation-reduction potential of the electrolytes.

Thermal properties of the conjugated polymer and conversion to poly(*p*-phenylene)

The thermal behavior of the conjugated polymer was evaluated by TG and DSC (see the Supplementary Information for DSC and TG curves). The glass transition temperature (T_g) was 210 °C. Weight loss, which was due to the loss of ethoxycarbonyl groups, was observed at 260 °C in both nitrogen and air. The TG profile in nitrogen shows that the conjugated polymer loses ~41% of its original mass upon heating at 450 °C. This weight loss is close to the value expected for complete conversion to poly(*p*-phenylene). To demonstrate that the conjugated polymer was converted to poly(*p*-phenylene), pyrolysis experiments were conducted on the powder for subsequent spectroscopic analysis. To perform the pyrolysis experiments, the powder was heated under nitrogen at 300 °C for 1 h, and then analyzed by IR spectroscopy. Figure 6 shows IR spectra of the conjugated polymer powder before and after heating at 300 °C. In the powder heated at 300 °C, the IR spectrum did not show peaks at 2980 cm⁻¹ and 2930 cm⁻¹ due to C-H stretching of the ethyl group or at 1720 cm⁻¹ and 1230 cm⁻¹ due to the carbonyl group. A strong peak occurred at 800 cm⁻¹, due to the C-H out-of-plane deformation of the 1,4-disubstituted benzene ring. The peaks at 1470 cm⁻¹ and 1400 cm⁻¹ are due to ring stretching, and those at 780 cm⁻¹ and 690 cm⁻¹ are due to the C-H out-of-plane bending modes of the monosubstituted benzene end group unit. The peak at 1100 cm⁻¹ is assigned to the C-Cl stretching. No other IR peaks were apparent, indicating that the conjugated polymer was converted to poly(*p*-phenylene) with a regular structure.

CONCLUSIONS

Conjugated polymers were synthesized by Ni(0)-catalyzed coupling polymerizations of 3,6-di(4-chlorophenyl)-3,6-dihydrophthalic acid diethyl ester accompanied by isomerization of the 1,4-cyclohexadiene moiety into a 3,5-cyclohexadiene group. The conjugated polymer dissolved only at concentration of 1 wt% or less, even in hot organic solvents. The conjugated polymer also exhibited a λ_{max} at 430 nm in its absorption spectrum, and could be applied as a photo-sensitizer of solar cells by modifying an ITO/TiO₂ electrode with a dilute solution of the conjugated polymer. The conjugated polymer showed a glass transition temperature of 210 °C, and was converted by thermal treatment at 300 °C to poly(*p*-phenylene) with the elimination of ethoxycarbonyl groups.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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