Macromolecules **1995,** *28,* 8363–8367

Synthesis of Soluble Poly(arylenevinylene)s Carrying Various Heterocycles as Arylene Units

Hiroki Saito, Shigeyuki Ukai, Shouji Iwatsuki, Takahito Itoh, and Masataka Kubo*,†

Department of Chemistry for Materials, Faculty of Engineering, and Instrumental Analysis Center, Mie University, Kamihama-cho, Tsu 514, Japan

Received December 9, 1994; Revised Manuscript Received September 5, 1995®

ABSTRACT: The Wittig reactions of 2,5-bis(dodecyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) (**6c**) with thiophene-2,5-dicarbaldehyde (**1a**), selenophene-2,5-dicarbaldehyde (**1b**), tellurophene-2,5-dicarbaldehyde (**1c**), and benzo[*c*]thiophene-1,3-dicarbaldehyde (**1d**) were carried out to obtain poly(2,5-thiophenediylvinylene- (**7ac**), 2,5-selenophenediylvinylene- (**7bc**), 2,5-tellurophenediylvinylene- (**7cc**), and 1,3-benzo[*c*]thiophenediylvinylene-*alt*-2,5-bis(dodecyloxy)-1,4-phenylenevinylene)s (**7dc**), respectively. These polymers were characterized by ^{1}H NMR, IR, UV–vis, and elemental analysis. Their voltammetric and optical third-harmonic generation (THG) measurements were carried out.

Introduction

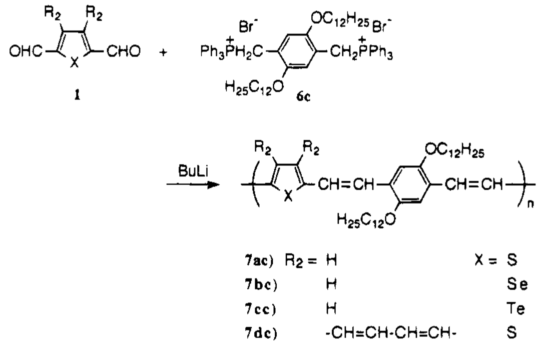
Poly(arylenevinylene)s are considered to be promising candidates for electrical and/or optical materials. Most of these polymers are neither fusible nor soluble in common solvents, making it difficult to process them into shaped articles. Several attempts have been made to prepare poly(arylenevinylene) films, including poly(1,4-phenylene-,[1–3] 2,6-disubstituted-1,4-phenylene-,[4–6] 1,4-naphthalene-,[7] 2,5-thienylene-,[8–10] 2,5-furylene-,[11,12] 2,5-selenophenediyl-,[13] 4,7-benzo[*b*]thiophenediyl-,[14] and 4,7-benzo[*b*]furandiylvinylene)s.[14] They were prepared successfully by the so-called sulfonium salt method. (Arylenedimethylene)bis(dialkylsulfonium halide) was reacted with base in aqueous solution to give a soluble precursor polymer. It was cast into film and converted to poly(arylenevinylene) by a thermal elimination reaction.

We were interested in a more general approach to prepare poly(arylenevinylene)s bearing various arylene units. Our idea was to use the Wittig reaction of 2,5-bis(alkyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) with heterocyclic dialdehyde compounds. This work describes the Wittig reactions between 2,5-bis(dodecyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) (**6c**) and four heterocyclic dialdehyde compounds **1** (Scheme 1).

Experimental Section

General Procedures. ^{1}H NMR spectra were measured with a JEOL EX-270 (270 MHz) nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard. IR spectra were measured with a Jasco IR-700 infrared spectrophotometer. UV–visible spectra were measured with a Jasco UVIDEC-403B spectrophotometer. Melting points were measured with a Büchi 510 capillary melting point apparatus. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G3000H and G2500H using tetrahydrofuran (THF) and standard polystyrenes as eluent and references, respectively. Elemental analysis was performed on Yanaco MT-2 CHN CORDER. Voltammetric measurement was carried out in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) at room temperature. Ag/AgCl, glassy carbon, and platinum wire were used as the reference, working, and third electrodes, respectively.

Scheme 1



Thiophene-2,5-dicarbaldehyde (1a). Compound **1a** was prepared from thiophene according to the method of Fringa et al.:[15] yield, 68%; mp 108–111 °C (lit.[15] mp 109–112 °C).

Selenophene-2,5-dicarbaldehyde (1b). To the mixture of selenophene[16] (7.2 g, 52 mmol), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (14.0 g, 120 mmol), and 30 mL of hexane was added 83 mL of 1.6 M butyllithium in hexane dropwise below 40 °C, and the reaction mixture was heated under reflux for 30 min. It was cooled to −40 °C, and *N,N*-dimethylformamide (DMF) (11.3 g, 155 mmol) was added via an air-tight syringe. The reaction mixture was allowed to warm to room temperature and poured into 300 mL of 10% hydrochloric acid solution. The mixture was neutralized with saturated sodium bicarbonate solution to separate the organic layer. The aqueous layer was extracted with chloroform, and the combined organic layer was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove the solvents. The residue was recrystallized from a mixture of benzene and hexane to give 5.3 g (51%) of **1b** as orange needles: mp 83.5–84.0 °C (lit.[17] mp 83 °C).

Tellurophene-2,5-dicarbaldehyde (1c). The synthesis procedure for **1c** was almost identical with the procedure for compound **1b**. To the mixture of tellurophene[18] (13.5 g, 75 mmol), TMEDA (20.0 g, 172 mmol), and 30 mL of hexane was added 100 mL of 1.6 M butyllithium in hexane dropwise below 40 °C, and the reaction mixture was heated under reflux for 30 min. It was cooled to −40 °C, and DMF (12.4 g, 170 mmol) was added via an air-tight syringe. The final product was recrystallized from a mixture of benzene and hexane to give 7.7 g (43%) of **1c** as orange needles: mp 86–87 °C; ^{1}H NMR (CDCl$_3$) δ 9.84 (s, 2H), 8.65 (s, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1608. Anal. Calcd for $C_6H_4O_2Te$: C, 30.58; H, 1.71. Found: C, 30.67; H, 1.64.

Benzo[*c*]thiophene-1,3-dicarbaldehyde (1d). The synthesis procedure for **1d** was almost identical with the procedure for compound **1b**. To the mixture of freshly prepared

---

[†] Instrumental Analysis Center.

® Abstract published in *Advance ACS Abstracts,* November 1, 1995.

0024-9297/95/2228-8363$09.00/0

benzo[c]thiophene[19] (2.1 g, 15 mmol), TMEDA (4.2 g, 36 mmol), and 20 mL of hexane was added 22 mL of 1.6 M butyllithium in hexane dropwise below 40 °C, and the reaction mixture was heated under reflux for 30 min. It was cooled to −40 °C, and DMF (3.0 g, 42 mmol) was added via an air-tight syringe. The final product was recrystallized from hexane to give 2.3 g (78%) of **1d** as yellow needles: mp 157−158 °C; ^{1}H NMR ($CDCl_3$) δ 10.40 (s, 2H), 8.4−8.3 (m, 2H), 7.6−7.5 (m, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1607. Anal. Calcd for $C_{10}H_6O_2S$: C, 63.14; H, 3.18. Found: C, 63.00; H, 3.15.

Diethyl 2,5-Bis(alkyloxy)terephthalate (3). The mixture of diethyl 2,5-dihydroxyterephthalate[20] (**2**) (2.0 g, 8.0 mmol), potassium carbonate (5.5 g, 40 mmol), 100 mL of DMF, and 1-bromohexane (3.0 g, 18 mmol), 1-bromooctane (3.5 g, 18 mmol), or 1-bromododecane (4.5 g, 18 mmol) was stirred for 5 h at 80 °C. It was poured into water and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and placed under reduced pressure. The residue was recrystallized from ethanol to give diethyl 2,5-bis(hexyloxy)terephthalate (**3a**), diethyl 2,5-bis(octyloxy)-terephthalate (**3b**), or diethyl 2,5-bis(dodecyloxy)terephthalate (**3c**).

3a: yellow needles; yield, 83%; mp 33−34 °C; ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 2H), 4.37 (q, J = 7.2 Hz, 4H), 4.00 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 22H), 0.90 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1697. Anal. Calcd for $C_{24}H_{38}O_6$: C, 68.22; H, 9.06. Found: C, 68.42; H, 9.15.

3b: yellow needles; yield, 89%; mp 38−40 °C; ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 2H), 4.37 (q, J = 7.2 Hz, 4H), 4.00 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 30H), 0.88 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1698. Anal. Calcd for $C_{28}H_{46}O_6$: C, 70.26; H, 9.69. Found: C, 70.18; H, 9.60.

3c: white needles; yield, 55%; mp 58−59 °C; ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 2H), 4.37 (q, J = 7.2 Hz, 4H), 4.00 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 46H), 0.88 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1659. Anal. Calcd for $C_{36}H_{62}O_6$: C, 73.18; H, 10.58. Found: C, 73.32; H, 10.49.

2,5-Bis(alkyloxy)-*p*-xylylene Alcohol (4). Into a suspension of lithium aluminum hydride (0.47 g, 12 mmol) in 10 mL of ether was added **3a** (2.5 g, 6.0 mmol), **3b** (2.9 g, 6.0 mmol), or **3c** (3.5 g, 6.0 mmol) in 60 mL of ether dropwise and heated under reflux for 30 min. The reaction mixture was cooled to 0 °C and water was added slowly. The mixture was repeatedly extracted with ether, and the extract was dried over anhydrous magnesium sulfate and placed under reduced pressure to give 2,5-bis(hexyloxy)- (**4a**), 2,5-bis(octyloxy)- (**4b**), or 2,5-bis(dodecyloxy)-*p*-xylylene alcohol (**4c**).

4a: white needles; yield, 90%; mp 97 °C; ^{1}H NMR ($CDCl_3$) δ 6.84 (s, 2H), 4.67 (s, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 16H), 0.90 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) ν_{OH} 3260. Anal. Calcd for $C_{20}H_{34}O_4$: C, 70.97; H, 10.12. Found: C, 71.06; H, 10.27.

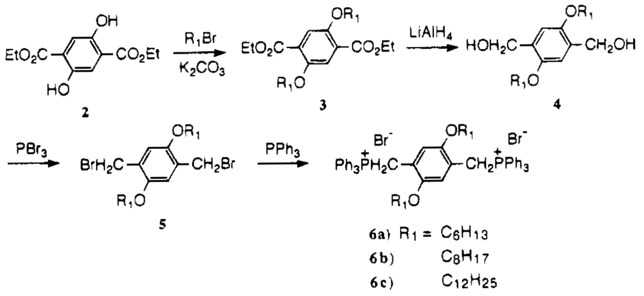
4b: white needles; yield, 86%; mp 99−100 °C; ^{1}H NMR ($CDCl_3$) δ 6.84 (s, 2H), 4.67 (s, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 24H), 0.89 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) ν_{OH} 3258. Anal. Calcd for $C_{24}H_{42}O_4$: C, 73.05; H, 10.73. Found: C, 73.23; H, 10.81.

4c: white needles; yield, 94%; mp 109−110 °C; ^{1}H NMR ($CDCl_3$) δ 6.84 (s, 2H), 4.67 (d, J = 8.4 Hz, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 40H), 0.88 (t, J = 6.6 Hz, 6H); IR (KBr, cm^{-1}) ν_{OH} 3320. Anal. Calcd for $C_{32}H_{58}O_4$: C 75.84; H, 11.53. Found: C, 75.77; H, 11.45.

2,5-Bis(alkyloxy)-*p*-xylylene Bromide (5). Into a suspension of **4a** (1.7 g, 5.0 mmol), **4b** (2.0 g, 5.0 mmol), or **4c** (2.5 g, 5.0 mmol) in 200 mL of benzene was added phosphorus tribromide (0.95 g, 3.5 mmol) in 10 mL of benzene and stirred for 5 h. The reaction mixture was washed with water, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was recrystallized from hexane to give 2,5-bis(hexyloxy)- (**5a**), 2,5-bis(octyloxy)- (**5b**), or 2,5-bis(dodecyloxy)-*p*-xylylene bromide (**5c**).

5a: white needles; yield, 88%; mp 88−86 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{20}H_{32}Br_2O_2$: C, 51.74; H, 6.95. Found: C, 51.78; H, 7.02.

Scheme 2



5b: white needles; yield, 76%; mp 85−89 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 16H), 0.91 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{24}H_{40}Br_2O_2$: C, 55.39; H, 7.75. Found: C, 55.53; H, 7.85.

5c: white needles; yield, 92%; mp 93−94 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.9−1.3 (m, 40H), 0.88 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{32}H_{56}Br_2O_2$: C, 60.76; H, 8.92. Found: C, 60.88; H, 8.98.

2,5-Bis(alkyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) (6). A mixture of triphenylphosphine (2.4 g, 9.2 mmol), 70 mL of ethanol, and **5a** (1.9 g, 4.0 mmol), **5b** (2.1 g, 4.0 mmol), or **5c** (2.5 g, 4.0 mmol) was stirred at room temperature for 15 h. It was placed under reduced pressure to remove the solvent, and the residue was recrystallized from benzene to give 2,5-bis(hexyloxy)- (**6a**), 2,5-bis(octyloxy)- (**6b**), or 2,5-bis(dodecyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) (**6c**).

6a: white plates; yield, 86%; ^{1}H NMR (DMSO-d_6) δ 7.9−7.6 (m, 30H), 6.50 (s, 2H), 4.87 (d, J = 13.9 Hz, 4H), 2.97 (t, J = 6.6 Hz, 4H), 1.3−1.0 (m, 16H), 0.84 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{24}H_{38}Br_2O_2P_2$: C, 68.02; H, 6.32. Found: C, 68.23; H, 6.25.

6b: white plates; yield, 78%; ^{1}H NMR (DMSO-d_6) δ 7.9−7.6 (m, 30H), 6.52 (s, 2H), 4.88 (d, J = 13.9 Hz, 4H), 3.00 (t, J = 6.6 Hz, 4H), 1.3−1.0 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{60}H_{70}Br_2O_2P_2$: C, 68.96; H, 6.75. Found: C, 68.88; H, 6.79.

6c: white plates; yield, 76%; ^{1}H NMR (DMSO-d_6) δ 7.9−7.6 (m, 30H), 6.51 (s, 2H), 4.88 (d, J = 13.9 Hz, 4H), 2.99 (t, J = 6.6 Hz, 4H), 1.3−1.0 (m, 40H), 0.86 (t, J = 6.6 Hz, 6H). Anal. Calcd for $C_{68}H_{86}Br_2O_2P_2$: C, 70.58; H, 7.49. Found: C, 70.54; H, 7.33.

Polymerization. To a solution of **6c** (0.579 g, 0.50 mmol) and **1a** (70.1 mg, 0.50 mmol), **1b** (93.5 mg, 0.50 mmol), **1c** (117.8 mg, 0.50 mmol), or **1d** (95.1 mg, 0.50 mmol) in 10 mL of THF was added 0.75 mL of 1.6 M of butyllithium in hexane, and the reaction mixture was stirred for 5 h at room temperature. The mixture was poured into ethanol to precipitate the polymer. It was dissolved in THF and poured into ethanol to precipitate the polymer again. The product was dried under reduced pressure to constant weight.

Results and Discussion

Effect of Alkyloxy Group on the Solubility of 6. Our idea for the preparation of soluble poly(arylenevinylene)s was to use the Wittig reactions of 2,5-bis(alkyloxy)-*p*-xylylenebis(triphenylphosphonium bromide)s **6** with heterocyclic dialdehyde compounds. Through the addition of an appropriate side group of compound **6**, the resulting polymers are expected to be soluble in organic solvents. Three phosphonium salts were prepared to investigate the effect of the alkyloxy group on solubility (Scheme 2). The solubilities of **6a**, **6b**, and **6c** in various solvents are summarized in Table 1. Compound **6c** is the most soluble, even dissolving in THF. Thus, we used compound **6c** for the Wittig reaction.

Characterization. The polymerization results are summarized in Table 2. All reactions took place in a homogeneous state. The polymers obtained are soluble

Table 1. Solubilities[a] of 6a, 6b, and 6c

		solvent				
compound	alkyloxy	ethanol	DMSO	chloroform	THF	ether
6a	hexyloxy	+	+	+	−	−
6b	octyloxy	+	+	+	−	−
6c	dodecyloxy	+	+	+	+	−

[a] +, soluble; −, insoluble.

Table 2. Polymerization Results

entry	reactants		product	yield (%)	$10^{-4}M_n$[a]	anal. found (calcd) C	anal. found (calcd) H
1	**1a**	**6c**	**7ac**	52	1.2	78.79 (78.84)	9.89 (10.10)
2	**1b**	**6c**	**7bc**	56	1.1	73.09 (72.93)	9.49 (9.34)
3	**1c**	**6c**	**7cc**	65	0.7	67.49 (67.67)	8.85 (8.67)
4	**1d**	**6c**	**7dc**	78	2.9	80.55 (80.20)	9.96 (9.61)

[a] Determined by GPC.

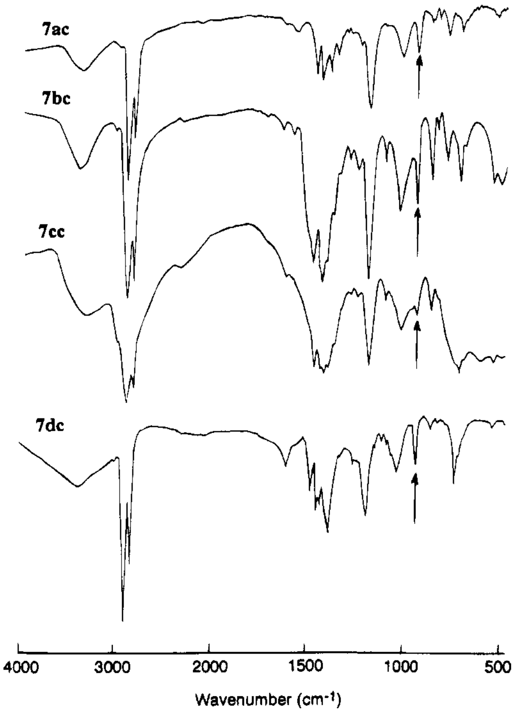


Figure 1. IR spectra of poly(arylenevinylene)s **7** (KBr).

in chloroform and THF. Dissolution of **7ac**, **7bc**, and **7cc** in THF produced a red solution and dissolution of **7dc** in THF produced a purple one. Elemental analyses were in good agreement with those for the expected structures. The ^{1}H NMR spectra of **7** exhibit absorption peaks at 7.5−6.5 (m, vinylene and aromatic/heterocyclic protons), 3.8 (br s, OCH_2), and 2.0−0.8 (m, CH_2 and CH_3). The molecular weights of compounds **7** were found to be 7000−29000 as polystyrene standards. Since the ^{1}H NMR spectra of **7** show no peaks assignable to terminal groups (aldehyde or triphenylphosphoniomethyl groups), the degree of polymerization of these polymers was considered to be more than 50. The IR spectra of **7ac**, **7bc**, **7cc**, and **7dc** are shown in Figure 1. The products exhibit absorption bands around 935 cm^{-1} due to the C−H out-of plane bending of the *trans*-vinylene. It was concluded that the Wittig reactions between **1** and **6** gave corresponding poly(arylenevinylene)s **7**.

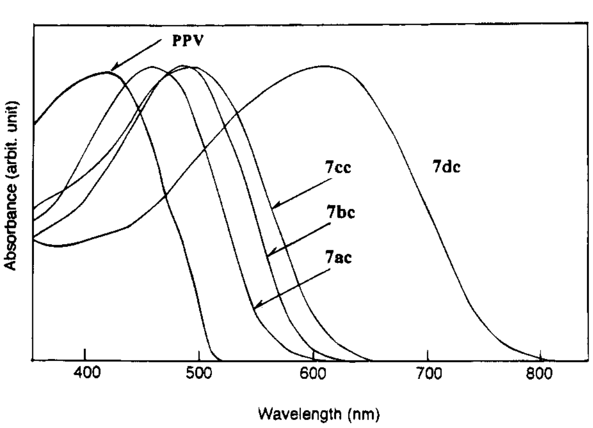


Figure 2. UV−visible spectra of poly(arylenevinylene)s **7** in THF and of PPV thin film.

UV−vis Spectra. The UV−visible spectra of **7ac**, **7bc**, **7cc**, and **7dc** were measured in THF solution, as shown in Figure 2. The UV−vis spectrum of a thin film of poly(1,4-phenylenevinylene) (PPV) prepared according to the method of Gagnon et al.[3] is also shown in Figure 2. The optical bandgaps of **7ac**, **7bc**, **7cc**, **7dc**, and PPV were found to be 2.4, 2.3, 2.2, 1.7, and 2.7 eV, respectively, as summarized in Table 3. Poly(arylenevinylene)s **7** were found to have smaller bandgaps than PPV. The optical bandgap decreased in the order **7ac** > **7bc** > **7cc** ≫ **7dc**. This trend is probably a reflection of the electronegativity of the heterocycles. The pK_a's of the 2-carboxylic acids of thiophene, selenophene, and tellurophene are reported to be 3.53, 3.60, and 3.97, respectively.[21] Poly(benzo[*c*]thiophene) has the smallest bandgap (≈1 eV) of any known conjugated organic polymer.[22] It was concluded that the introduction of the benzo[*c*]thiophene unit is effective in reducing the optical bandgap of the resulting poly(arylenevinylene). Very thin films (0.02−0.06 mm) of **7** were cast onto silica glass and kept under air at room temperature for 45 days, and their absorbances were measured. It was found that these films were stable under these conditions.

Electrochemical Properties. The voltammetric measurements of poly(arylenevinylene)s **7** were carried out in dichloromethane solution containing tetrabutylammonium perchlorate (0.1 mol/L) at room temperature. The voltammograms are shown in Figure 3. These polymers exhibit an oxidation peak, as summarized in Table 3. Obviously, a poly(arylenevinylene) with a smaller bandgap exhibits lower oxidation potential.

Optical Third-Harmonic Generation. Third-harmonic generation (THG) measurements were performed at 1.90 μm using difference frequency generation of a Q-switched Nd:YAG laser and a tunable dye laser.[23] The measured third-harmonic intensity at 1.90 μm for the **7ac** film as a function of the incident angle is shown in Figure 4, together with that for a silica glass substrate of 0.5 mm thickness. The third-harmonic intensity from the glass substrate shows the so-called Maker fringe pattern, corresponding to consecutive optical path length variations (Figure 4a). The intensity from the **7ac** thin film shows a monotonic function of the incident angle (Figure 4b). The third-order susceptibility, $\chi^{(3)}$, of the thin-film sample was calculated by the following equation:[23]

$$\chi^{(3)} = (2/\pi)\chi_s^{(3)}(I_{3\omega}^{1/2}/l)(I_{3\omega,s}^{1/2}/l_{c,s})$$

where l is the sample thickness, $\chi_s^{(3)}$ and $l_{c,s}$ are the third-order susceptibility and the coherence length of the fused silica glass substrate, respectively, and $I_{3\omega}$ and $I_{3\omega,s}$ are the measured peak intensity values in the THG patterns of the sample and the fused silica glass,

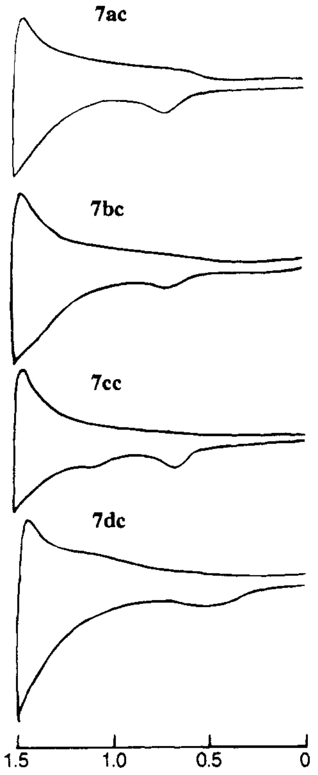


Figure 3. Cyclic voltammograms of poly(arylenevinylene)s 7 in dichloromethane at a scan rate of 100 mV/s.

Table 3. Physical Properties of 7ac, 7bc, 7cc, and 7dc

polymer	bandgap (eV)	oxidation potential[a] (V)	$10^{11}\chi^{(3)}$ (esu)[b]
7aa	2.4	0.72	0.9
7bc	2.3	0.70	
7cc	2.2	0.69	1.1
7dc	1.7	0.52	1.5
PPV	2.6		0.7[c]

[a] Versus Ag/AgCl. [b] At 1.9 μm wavelength. [c] Value from ref 25.

respectively. For the calculation, a $\chi_s^{(3)}$ of 2.8×10^{-14} esu was used for fused silica glass, as reported by Meredith et al.[24] The refractive index difference between **7** and silica glass was neglected. The values obtained for poly(arylenevinylene)s **7** are summarized in Table 3, together with that of PPV.[25] In the case of **7bc**, an accurate $\chi^{(3)}$ was not obtained because of film roughness. Since **7dc** has high absorption in the wavelength region of the third harmonic ($\lambda = 633$ nm), the third-order susceptibility at the nonresonant wavelength cannot be properly estimated in this experiment. The evaluated susceptibilities of **7ac** and **7cc** are higher than that of PPV film, indicating that poly(arylenevinylene)s **7ac** and **7cc** are effective for nonlinear optical materials with easy processing.

It is said that $\chi^{(3)}$ of a π-conjugated polymer is enhanced through lengthening of the delocalized length. That is, $\chi^{(3)}$ has been reported to be proportional to the sixth power of the delocalization length, which is exhibited as W/E_g, where W is the bandwidth and E_g is the bandgap of the polymer.[26] Thus, the high susceptibilities of **7ac** and **7cc** can be explained by their small bandgaps.

Conclusions

Various heterocycles were successfully fused onto a poly(arylenevinylene) backbone by the Wittig reactions of 2,5-bis(dodecyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) with heterocyclic dialdehyde compounds. It was found that the bandgap of the resulting poly(arylenevinylene) is dependent on the nature of the heterocycle moiety. Polymers **7ac** and **7cc** are considered to be effective for nonlinear optical materials with easy processing. Although polymer **7dc** has small bandgap, the large absorbance around the third harmonic restricts its application as a third-order nonlinear optical material at 1.9 μm wavelength. Finally, this synthetic approach has the advantage of being able to introduce various heterocycles into poly(arylenevinylene)s.

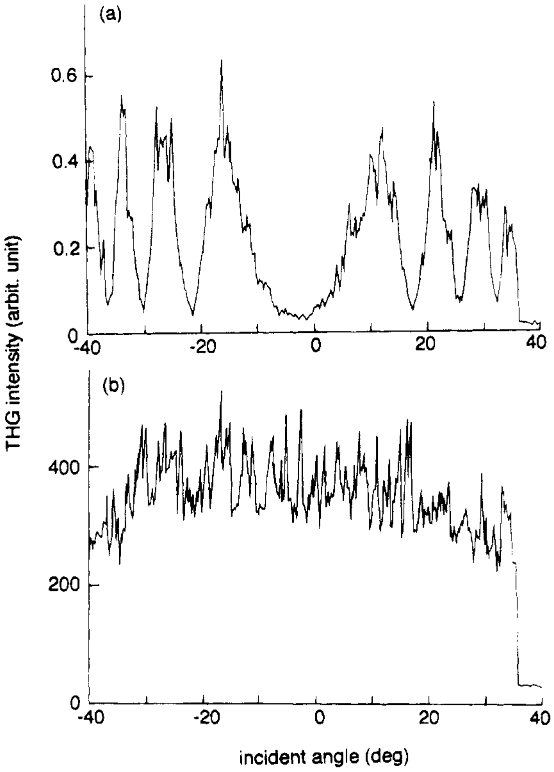


Figure 4. Measured third-harmonic intensities at 1.90 μm as a function of incident angle for (a) silica glass substrate of 0.5 mm thickness and (b) **7ac** thin film of 3 μm thickness.

Acknowledgment. The authors thank Dr. Tadanori Hashimoto, Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, for the THG measurements.

References and Notes

(1) Wessling, R. A.; Zimmerman, R. G. U.S. Patent 3401152, 1968.
(2) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.
(3) Gagnon, D. R.; Capstrain, J. D.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1984**, *12*, 293.
(4) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1985**, *26*, 362.
(5) Han, C. C.; Lenz, R. W.; Karasz, F. E. *Polym. Commun.* **1987**, *28*, 1041.
(6) Momii, T.; Tokito, S.; Tsutsui, T.; Saito, S. *Chem. Lett.* **1988**, 1201.
(7) Antoun, S.; Gagnon, D. R.; Karasz, F. E.; Lenz, R. W. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 503.
(8) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1987**, *28*, 229.
(9) Jen, K. Y.; Maxfield, M.; Shacklett, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309.
(10) Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448.

(11) Jen, K. Y.; Jow, T. R.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1113.

(12) Kim, J. C.; Murata, H.; Tsutsui, T.; Saito, S. *Nippon Kagaku Kaishi* **1992**, 399.

(13) Iwatsuki, S.; Kubo, M.; Kamei, N. *Chem. Lett.* **1992**, 1551.

(14) Sarker, A.; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Educ.* **1993**, *32*, 65.

(15) Feringa, B. L.; Hulst, R.; Likers, R.; Brandsma, L. *Synthesis* **1988**, 316.

(16) Mohmand, S.; Bargon, J.; Waltman, R. J. *J. Org. Chem.* **1983**, *48*, 3544.

(17) Paulmier, C.; Pastour, P. *Bull. Soc. Chim. Fr.* **1966**, 4021.

(18) Fringuelli, F.; Taticchi, A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 199.

(19) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *25*, 3932.

(20) Guha, P. C. *Chem. Ber.* **1939**, *72*, 1359.

(21) Fringuelli, F.; Marino, G.; Taticchi, A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1738.

(22) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.

(23) Tomaru, S.; Kubodera, K.; Zembutsu, S.; Takeda, K.; Hasegawa, M. *Electron Lett.* **1987**, *23*, 595.

(24) Meredith, G. R.; Bauchalter, B.; Hanzlik, C. *J. Chem. Phys.* **1983**, *78*, 1533.

(25) Kaino, T.; Kubodera, K.; Tomaru, S.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Electron. Lett.* **1987**, *23*, 1095.

(26) Agrawal, G. P.; Cojan, C.; Hanzlik, C. *Phys. Rev.* **1976**, *B17*, 776.

MA946406B