Synthesis and Properties of Three Kinds of Phenylenevinylene Copolymers with Dialkoxyphenylene Units

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ABSTRACT: Two random copolymers, poly(*p*-phenylenevinylene-*co*-2,5-didodecyloxy-*p*-phenylenevinylene) and poly(2,5-dimethoxy-*p*-phenylenevinylene-*co*-2,5-didodecyloxy-*p*-phenylenevinylene), were synthesized via the chlorine precursor route followed by thermal elimination. One alternating copolymer, poly(*p*-phenylenevinylene-*alt*-2,5-didodecyloxy-*p*-phenylenevinylene), was prepared via the Heck coupling reaction. The effects of molar ratio of monomers on yield and composition of the precursor copolymers were studied. The two precursor copolymers and the alternating copolymer were characterized by gel permeation chromatography, differential scanning calorimetry, elemental analysis, and infrared spectroscopy. The UV-visible absorption spectra and photoluminescence spectra, as well as solubility and conductivity of these copolymers, were compared. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 937–946, 1998

INTRODUCTION

Poly(*p*-phenylenevinylene)(PPV) and its derivatives are receiving considerable attention due to their high electrical conductivity,[1] luminescence,[2] and third-order nonlinear optical properties.[3] PPV and its derivatives may offer several advantages over the traditional inorganic materials used in the present generation of light-emitting diodes. First, PPVs are processable as a precursor, and they can be deposited over large areas as high-quality thin films. Second, changes in electric, luminescent, and mechanical properties and solubility can be effected by the introduction of substituents[4-8] or copolymerization.[9-11] Doi and coworkers[6] and Barashkov and colleagues[7] found out separately that introduction of long alkoxy groups as substituents of PPV plays an important role in improving the solubility and photoluminescence (PL) of PPV. Jin and coworkers[8] reported the effect of long alkoxy-substituted phenylenevinylene (PV) units on shift of emission spectrum and on change of conductivity. Lenz and coworkers[9] studied the synthesis of poly(*p*PV-*co*-dialkoxy-*p*-PV) via the Wessling method or water-soluble precursor method, and indicated that introduction of a small amount of 2,5-dialkoxy-substituted PV units into PPV can obviously increase the conductivity of PPV doped by I$_2$. Kraft and colleagues[10] and Holmes and coworkers[11] showed separately that poly(*p*-PV-*co*-2,5-dimethoxy-*p*-PV) synthesized via water-soluble precursor changed the photoluminescent properties of PPV. Swatos and Gorden[12] and Wudl and coworkers[13] successively used the chlorine precursor route instead of the Wessling method to synthesize PPV and its derivatives. Bao and coworkers[14] reported the synthesis of alternating copolymers of (PV-*alt*-2,5-dihexadecyloxy-PV).

This article deals with the synthesis of two random copolymers—poly(*p*-PV-*co*-2,5-didodecyloxy-*p*-PV) [P(PV-PDDOPV)] (copolymer **I**) and

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poly(2,5-dimethoxy-*p*-PV-*co*-2,5-didodecyloxy-*p*-PV) [P(DMOPV-DDOPV)] (copolymer **II**)—using the chlorine precursor route and one alternating copolymer of P(PV-*alt*-DDOPV) (copolymer **III**) via the Heck coupling reaction route, as well as study of solubility, conductivity, and photoluminescent properties of the three copolymers.

EXPERIMENTAL

Materials

All of the reagents and solvents were chemically pure. *t*-Butanol and petroleum ether (boiling point: 60–90°C) were dried overnight over a 5 Å molecular sieve. A complex of potassium *t*-butoxide/*t*-butanol was prepared as follows: *t*-butanol was reacted with metallic potassium under reflux until completely dissolved. Excess *t*-butanol was distilled off until the appearance of crystals. Then, dry petroleum ether was added, and distillation was continued until 98°C. The residue was a 1 : 1 complex, and its concentration was determined by standard acid.

Monomers

1,4-Bis(chloromethyl)benzene was synthesized as follows: 120 g chloromethyl ether, 140 g benzyl chloride, and 90 g anhydrous zinc chloride were reacted at 60°C with introduction of dry HCl gas for 70 min. After cooling, the reaction mixture was filtered and washed with 40°C water and then with 70°C water, several times each. The crude product was dried and recrystallized twice with ethanol. Colorless needle crystal was obtained with 48% yield and a melting point (m.p.) of 100–101°C.

1,4-Dimethoxybenzene was obtained by adding 12 ml dimethyl sulfate to a solution of 11 g *p*-hydroxyphenol, 11 g NaOH, and 70 mL water at 10°C with vigorous stirring for 5 min. After cooling, the product was crystallized, filtered, washed, and dried with 90% yield and an m.p. of 56–57°C.

1,4-Didodecyloxybenzene was prepared by a reaction of KOH powders with *p*-hydroxyphenol in dimethylsulfoxide at room temperature with vigorous stirring for 1 h, followed by dropping 1-bromododecane at 70°C within 3 h and then heating at 75°C for 2 h. After cooling, the precipitate was recrystallized from isopropanol. The white flake product was obtained with 70% yield and an m.p. of 72–73°C.

1,4-Bis(chloromethyl)-2,5-dimethoxybenzene was prepared in the following way: to a mixture of 600 mL dioxane, 100 mL concentrated hydrochloric acid, and 0.75 mol of 1,4-dimethoxybenzene at 50–60°C was added 150 mL formalin within 1.5 h, while introducing dry HCl gas. The reaction was continued for 3 h. Then, 450 mL hydrochloric acid was added. After cooling, the precipitate was filtered and recrystallized from acetone. White crystals were obtained with an m.p. of 168–169°C and 60% yield. Elemental analysis (%): C 51.25 (51.09), H 5.07 (5.14), Cl 30.22 (30.16). Data in parentheses are the calculated values.
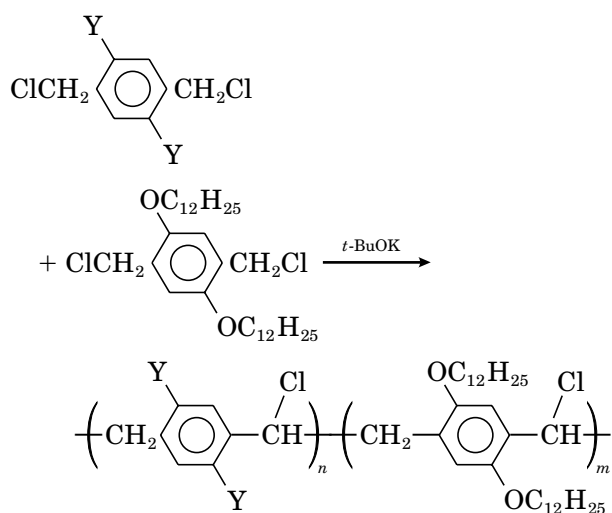
1,4-Bis(chloromethyl)-2,5-didodecyloxybenzene was synthesized as follows: 0.07 mol of 1,4-didodecyloxybenzene in 100 mL dioxane was reacted with dry HCl gas at 80°C, while dropping 30 mL formalin within 1 h. After reaction for 10 h, 150 mL water was added. The precipitate was filtered, dried, and recrystallized from $CHCl_3$. The purified product was white needle crystals with an m.p. of 83–84°C and 30% yield. Elemental analysis (%): C 70.58 (70.72), H 10.56 (10.31), Cl 12.96 (13.08).

1,4-Dibromo-2,5-didodecyloxybenzene was prepared in the following way: to a solution of 1,4-didodecyloxybenzene in CCl_4, a 10% excess of bromine was dropped in an ice bath. The mixture was stirred at room temperature for 5 h. Then, the reaction was terminated by adding a NaOH solution, and the reaction mixture was extracted with dichloromethane three times. The organic layer was dried with anhydrous $MgSO_4$. After distilling off the solvent, white flake solid was obtained with 60% yield and an m.p. of 80–81°C. Elemental analysis (%): C 59.70 (59.60), H 8.33 (8.60).

1,4-Divinylbenzene was obtained by first bromination of divinylbenzene, followed by reaction with zinc powder as follows: to a solution of 170 g divinylbenzene in 500 mL CCl_4, 320 g bromine was added dropwise with stirring at 20–25°C until the bromine color remained for more than 15 min. Two portions of 10 mL divinylbenzene were added at 15 min intervals. After the disappearance of the bromine color, the mixture was cooled to 0°C and stirred for 1 h. The precipitate was filtered, dried, and recrystallized with benzene several times. The white crystalline product was tetrabromo-1,4-divinylbenzene with 50% yield and a m.p. of 163–164°C. Tetrabromo-1,4-divinyl-

benzene (58.2 g) and p-methoxyphenol (0.5 g) were dissolved in a mixture of 300 mL dioxane and 26 mL water. The solution was heated to 85°C. Then, 19 g zinc powder was added within 15 min, and the mixture was stirred at 95°C for 5 min and cooled to 20°C. Excess zinc powder was filtered. The filtrate was combined with 500 mL 1,2-dichloroethane and washed with water. The organic layer was dried with anhydrous Na_2SO_4 and distilled under reduced pressure. The distillate at 48°C/l mm Hg was 1,4-divinylbenzene with an m.p. of 25–26°C.

Random Copolymerization via the Chlorine Precursor Route

where Y represents OCH_3 or H.

1,4-Bis(chloromethyl)benzene or 1,4-bis(chloromethyl)-2,5-dimethoxybenzene and 1,4-bis-(chloromethyl)-2,5-didodecyloxybenzene were dissolved in xylene. After purging with nitrogen, the solution was heated to 100°C and a stoichiometric amount of potassium t-butoxide/t-butanol complex was added with stirring. After reacting for 12 h, the reaction mixture was precipitated in a large amount of methanol, filtered, and washed with a water/methanol solution. After extracting with hot methanol for 24 h, the precipitate, which was the precursor of random copolymer **I** or **II,** was vacuum-dried and weighed.

Conversion of monomers (C_m) can be calculated by titration of the alkali consumed during polymerization with standard hydrochloric acid using the following equation:

$$C_m(\%) = (M_B V_B - M_A V_A)$$
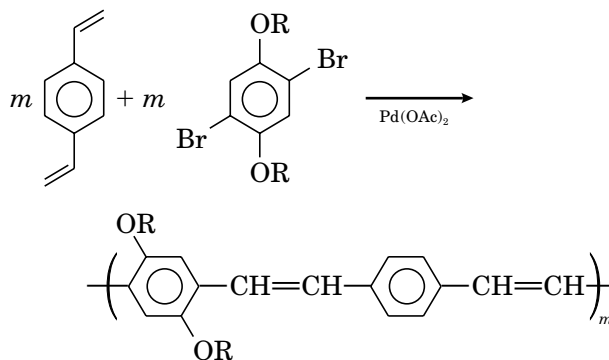$$\times 100/\text{mol of monomers} \quad (1)$$

where B represents t-BuOK and A represents standard hydrochloric acid.

Yield of the precursor copolymer (Y) can be obtained by the weighing method and calculated as follows:

$$Y_p(\%) = \text{Wt}_{\text{precursor}} \times 100/[\text{mol}_a(MW_a - 36.5) + \text{mol}_b(MW_b - 36.5)] \quad (2)$$

where a represents monomer a and b represents monomer b.

Alternating Copolymerization via the Heck Coupling Reaction

25 mmol dry triethylamine, 10 mmol 1,4-divinylbenzene, 10 mmol 1,4-dibromo-2,5-didodecyloxybenzene, 0.4 mmol palladium acetate, and 2 mmol triphenyl phosphine were dissolved in dry dimethylformamide and reacted under nitrogen atmosphere at 100°C for 15 h. The reaction product was precipitated in methanol, filtered, redissolved in $CHCl_3$, and then precipitated in acetone. The precipitate was extracted with hot methanol and vacuum-dried. The product is the alternating copolymer P(PV-alt-DDOPV) (copolymer **III**).

Thermal Elimination of the Precursor to Form the Random Copolymer

The precursor of random copolymer **I** or **II** was treated at 140°C for 6 h under vacuum to eliminate HCl, thus forming random copolymer **I** or **II.**

Characterization

Infrared spectra were taken by Shimadzu IR-435 infrared spectrophotometer using KBr pellets or cast film. Ultraviolet (UV)-visible spectra were obtained by Shimadzu UV-240 spectrophotometer. The differential scanning calorimetry (DSC) curve was conducted by a CDR-1 differential scanning calorimeter using a heating rate of 10°C min^{-1} under nitrogen atmosphere. C, H contents were determined by CHN-600 elemental analysis apparatus made by Leco Co. Chlorine content was determined by the oxygen flask combustion method. Gel permeation chromatography was performed in a Waters 150 apparatus with a UV detector using tetrahydrofuran as eluent and monodispersed polystyrene as a standard. Conductivity was measured by a SZ-85 four-probe apparatus (when $\sigma \geq 10^{-2}$ S cm^{-1}) or by a DDS-IIA conductometer (when $\sigma < 10^{-2}$ S cm^{-1}). PL spectra were obtained by a Shimadzu RF-540 fluorescence spectrophotometer.

Composition of copolymer **I** or **II** can be calculated from the C content determined from elemental analysis according to the following equations:

$$C(\%) = [32x + 10(1 - x)] \times 12$$
$$\times 100/(xMW_{\text{DDOPV}} + (1 - x)MW_{\text{DMOPV}}) \quad (3)$$
$$C(\%) = [32x + 8(1 - x)] \times 12$$
$$\times 100/(xMW_{\text{DDOPV}} + (1 - x)MW_{\text{PV}}) \quad (4)$$

where 32, 10, and 8 are the number of carbon atoms for DDOPV, DMOPV, and PV, respectively. Twelve is the atomic weight of C, and x is the mol fraction of DDOPV.

RESULTS AND DISCUSSION

Random Copolymer I [P(PV-*co*-DDOPV)]

Table I lists the effect of monomer molar ratio of DDOPV/PV on the conversion of monomers (C_m), yield (Y_p), composition, molecular weight, and molecular weight distribution of the precursor copolymer **I**. It can be seen that both monomer conversion and yield increase with DDOPV mol % in monomers. This implies that DDOPV is easier to copolymerize than PV. When the DDOPV mol % in monomers is plotted against DDOPV content of the precursor copolymer, a curve deviated from the diagonal line was obtained (Fig. 1). This fact

may be attributed to the higher activity of DDOPV monomer than that of PV monomer, due to the electron-repelling effect of alkoxy groups. The molecular weight of precursor copolymer **I** is in the range of $5-8 \times 10^4$ and the polydispersity index (PDI) about 4. The molecular weight of the precursor copolymer **I** seems to increase with DDOPV content; however, because the molecular weight of the DDOPV unit is higher than that of the PV unit, the degree of polymerization calculated tends to decrease with increasing DDOPV content (Table I).

UV-visible absorption spectrum of precursor copolymer **I** showed an absorption peak at 300 nm for the phenyl ring and no absorption at long wavelength, which demonstrates the absence of long conjugated segments. Infrared (IR) absorption of precursor copolymer **I** indicated strong absorption at 1518, 1031, 720, and 680 cm^{-1} corresponding to the vibration of phenyl ring, ϕ—O—CH$_2$ group, long alkyl group, and C—Cl group. The intensity of absorption peak for the long alkyl group increases with the increment of DDOPV content (Fig. 2), where the intensity of absorption peak for the phenyl group at 1518 cm^{-1} was taken as reference.

The glass transition temperature and decomposition temperature of precursor copolymer **I** obtained from DSC curves were listed in Table II. T_s is the glass transition temperature of the long dodecyl group that is situated in the range of 70–74°C. T_g of the main chain decreases obviously with increasing DDOPV content, probably due to the introduction of long soft dodecyloxy groups to the phenyl ring as side groups, which act as interplasticizers. Decomposition temperature decreases with increasing DDOPV content too, because the introduction of long side groups destroys the regularity of PPV and lowers packing density.

Precursor copolymer **I** can be completely transformed to the conjugated copolymer by thermal treatment at 140°C for 6 h under vacuum *via* the elimination reaction of HCl. The IR spectrum of the product exhibited absorption peak at 960 cm^{-1} for the *trans* double bond and the absorption peak at 3010 cm^{-1} for vibration of C—H of olefin, whereas the absorption peak at 684 cm^{-1} for C—Cl disappeared after thermal elimination.

Copolymer **I** containing more than 90 mol % DDOPV can be dissolved in chloroform completely, 90% of the copolymer containing 75 mol % can be dissolved, and only 58% of the copolymer

Table I Effect of Monomer Molar Ratio on Conversion, Yield, Composition, and Molecular Weight of Precursor Copolymer I

DDOPV/PV in Monomer (Molar Ratio)	DDPOV/PV in Polymer (Molar Ratio)	C_m (mole %)	Y_p (wt %)	$M_n \times 10^{-4}$	PDI	DP
DDOPV	PDDOPV	89	68	8.2	4.15	162
95/5	96.9/3.1	83	64	—	—	—
90/10	92.3/7.7	75	60	7.8	3.86	186
80/20	85.0/15.0	75	60	—	—	—
70/30	74.7/25.3	70	53	6.5	4.30	214
60/40	69.2/30.8	64	49	—	—	—
50/50	61.5/38.5	60	41	4.9	4.0	196
20/80	35.7/64.3	54	38	—	—	—
PPV	PPV	50	36	—	—	—

DP, degree of polymerization.

containing 36 mol % can be dissolved. The soluble part may contain more DDOPV units and lower molecular weight than the insoluble part, because the more DDOPV units that are in the random copolymer chains, the higher the solubility.

UV-visible spectra of PPV, PDDOPV, and copolymer **I** films obtained after thermal elimination (Fig. 3) show that the wavelengths of maximum absorption peaks are located around 400 and 490 nm for PPV and PDDOPV, respectively. The red shift of the latter is due to the electron-donating effect of dodecyloxy groups. It is surprising to note that the copolymer with 70 or 85 mol % DDOPV content exhibits the absorption spectrum similar to that of PPV. The result needs further study. However, the PL spectrum of copolymer **I** changes with DDOPV content (Fig. 4). The wavelength of the emitting peak of the copolymer shifts to red, whereas the intensity of the emitting peak increases as the DDOPV content increases. The former phenomenon may be explained by the change of effective conjugated length, whereas the latter fact may be due to the presence of dodecyloxy groups that prevent the polarons from being captured. This results in decreasing the proportion of the nonradiative process.
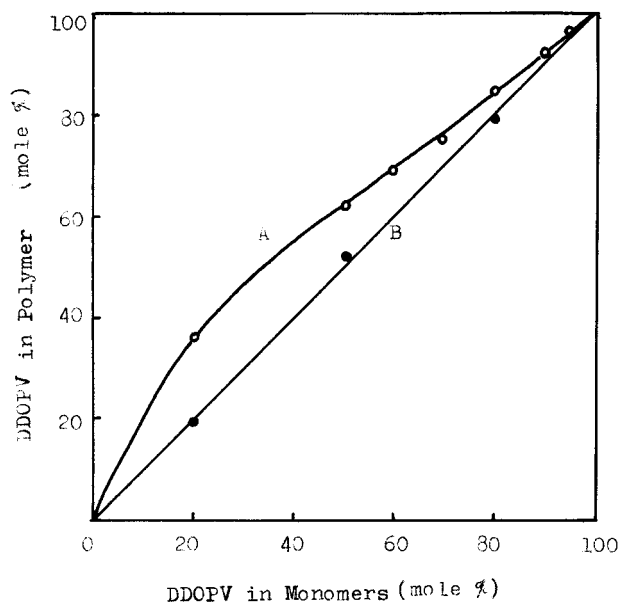

Figure 1 Relationship between charging DDOPV mole % and DDOPV content of the random copolymers: A-P(PV-*co*-DDOPV) and B-P(DMOPV-*co*-DDOPV).
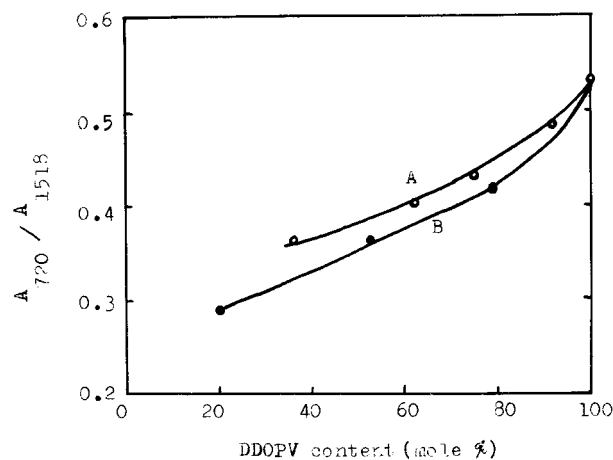

Figure 2 Ratio of absorption peak intensity at 720 cm^{-1} and 1518 cm^{-1} *versus* DDOPV content of the random copolymers: A-P(PV-*co*-DDOPV) and B-P(DMOPV-*co*-DDOPV).

**Table II DSC Data of Precursor Copolymer I
[P(PV-*co*-DDOPV)]**

DDOPV/PV (Molar Ratio)	T_s (°C)	T_g (°C)	T_d (°C)
PDDOPV	70	150	400
92.3/7.7	72	158	442
74.7/25.3	74	161	470
61.5/38.5	73	164	483
35.7/64.3	73	170	510
PPV	—	—	550

Table III lists the conductivities of copolymer **I** films doped by different dopants. The doping effect of I_2 or $FeCl_3$ on PPV is very poor, probably because PPV has a high ionization potential or oxidation potential, and also because I_2 is difficult to diffuse into the PPV film. However, if the PPV film was changed to copolymer **I** containing a small amount of DDOPV units, conductivity of the copolymer doped with I_2 or $FeCl_3$ raises notice-
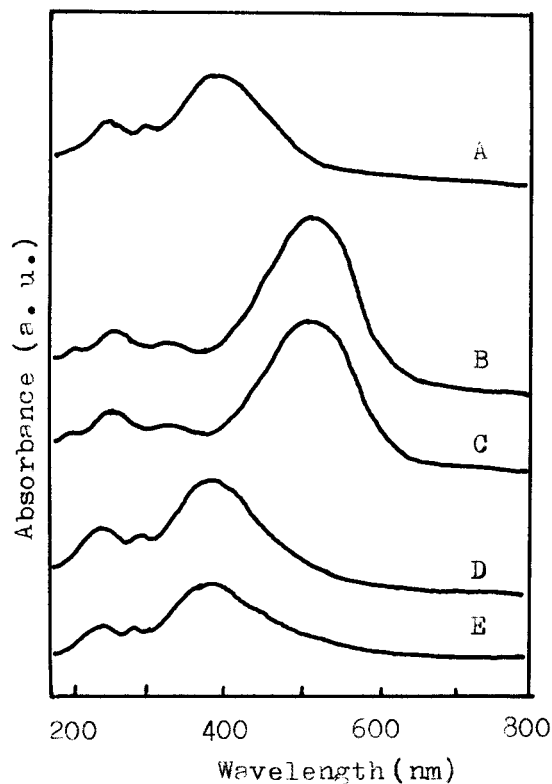

Figure 3 UV-visible spectra of PPV (A), PDDOPV (B), P(DMOPV-*co*-DDOPV) containing 78.6 mole % DDOPV (C), P(PV-*co*-PDDOPV) containing 85 mole % DDOPV (D), and 69.2 mole % DDOPV (E).
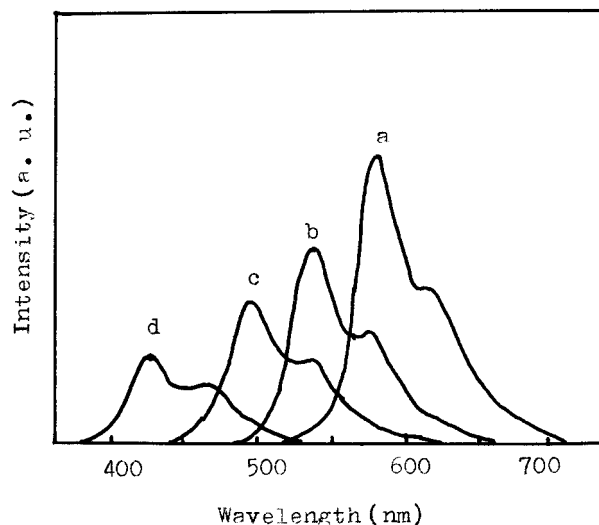

Figure 4 PL spectra of PDDOPV (a) and P(PV-*co*-DDOPV) containing 85 mole % PDDOPV (b), 74.7 mole % DDOPV (c), and 35.7 mole % DDOPV (d).

ably. This phenomenon may be attributed to the introduction of electron-donating alkoxy groups on the phenylene ring, which decreases the ionization potential and favors the oxidation with weak oxidant, thus resulting in increasing conductivity. Conductivity of doped copolymer **I** increases with copolymerized DDOPV, and the efficiency of dopants decreases in the following order: $I_2 > FeCl_3 > H_2SO_4 > O_2$.

Alternating Copolymer III (PV-*alt*-DDOPV)

Copolymer **III,** obtained by the Heck coupling reaction, possesses the alternative structure of PV and DDOPV, which exhibits quite different properties from those with random structure. Gel per-

Table III Conductivity of P(PV-*co*-DDOPV) Doped^a with Different Dopants

DDOPV/PV (Molar Ratio)	σ (S cm^{-1})			
	I_2	$FeCl_3$	H_2SO_4	O_2
PDDOPV	15.0	10.4	2.6	5×10^{-4}
92.3/7.7	10.0	2.6	1.1	3×10^{-5}
85.0/15.0	7.9	0.8	0.8	2×10^{-5}
69.2/30.8	5.6	0.26	0.06	—
35.7/64.3	0.16	0.08	—	—

^{a} The polymers were doped with Br_2 or I_2 vapor until equilibrium, or doped by immersion in 1% $FeCl_3$ (nitormethane solution) or concentrated H_2SO_4 until equilibrium.
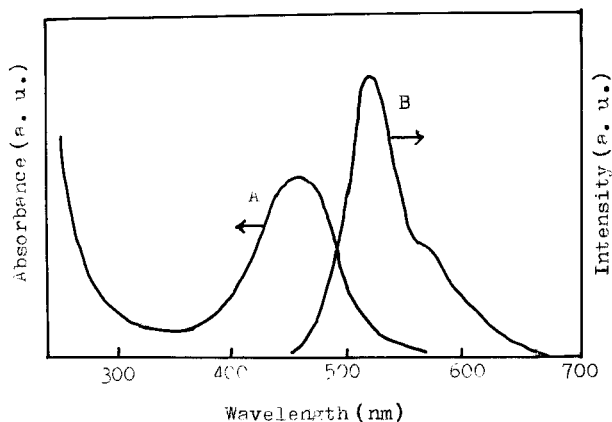
Figure 5 UV-visible absorption spectrum (A) and PL spectrum (B) of alternating copolymer **III.**

meation chromatography analysis of the alternating copolymer showed that M_n and M_w reached 1.4×10^5 and 3.1×10^5, respectively. The PDI is equal to 2.2 and the degree of polymerization is 640. These data indicated that alternating copolymer **III** possesses a much higher molecular weight and less polydispersity than random copolymer **I.**

Alternating copolymer **III** exhibits very good mechanical properties. Its film is strong, tough, and can be stretched. It can be dissolved in chloroform or tetrahydrofuran completely. The film of copolymer **III** doped with I_2 showed a conductivity of 0.5 S cm^{-1}.

Figure 5 illustrates the UV-visible absorption spectrum and PL spectrum of the alternating copolymer. The former is different from that of random copolymer **I** (Fig. 3). The wavelength of the maximum absorption peak is 460 nm, which is located between those of PPV (400 nm) and PDDOPV (490 nm). This is ascribed to the absence of PPV and PDDOPV segments. However, its PL spectrum is similar to that of random copolymer **I** with the near composition. The wavelength of the emitting peak is situated at 510 nm. The DSC curve of alternating copolymer **III** is quite different from that of random copolymer **I** (Fig. 6). It can be noted that no glass transition temperature of the long alkyloxy side group (T_s) exists at 70–75°C in the case of alternating copolymer, but two endothermic peaks appear at about 110°C and 240°C. Disappearance of T_s is due to the impossibility of the side groups of copolymer **III** to associate, whereas the two endothermic peaks may be attributed to the liquid crystalline behavior of the alternating copolymer. Bao and coworkers[14] reported the liquid crystalline behav-

ior of the alternating copolymer of PV and 2,5-dihexadecyloxy-*p*-PV.

Random Copolymer II [P(DMOPV-*co*-DDOPV)]

Table 4 lists the effect of monomer molar ratio of DMOPV/DDOPV on monomer conversion, yield, composition, molecular weight, and polydispersity of precursor copolymer **II.** It can be seen that the molar ratio of monomers showed little effect on C_m, Y_p, and composition of copolymer **II.** This case is quite different from the case of synthesis of copolymer **I** (Fig. 1). It implies that the reactivities of DMOPV and DDOPV are nearly the same. Hence, both C_m and Y_p are relatively higher than those in the copolymerization of PV and DDOPV. The molecular weight of the precursor of copolymer **II** seems to increase with the DDOPV monomer used, but the degree of polymerization calculated decreases with increasing DDOPV monomer used in copolymerization, because the molecular weight of DDOPV is higher than that of DMOPV. However, the PDI of precursor copolymer **II** is about 3, which is lower than that of copolymer **I.**

As in the case of copolymer **I,** the UV-visible spectrum of precursor copolymer **II** showed an absorption peak at 300 nm for phenyl ring and no absorption at the long wavelength for conjugated chain. IR spectrum of precursor copolymer **II** exhibited strong absorption at 1518, 1031, 720, and
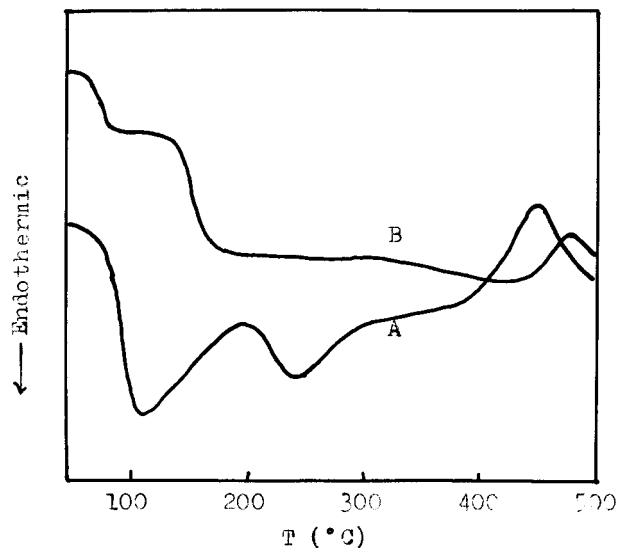

Figure 6 DSC curves of alternating copolymer (A) and random copolymer **I** containing 61.5 mole % DDOPV (B).

Table IV   Effect of Monomer Molar Ratio on Conversion, Yield, Composition, and Molecular Weight of Precursor Copolymer II

DDOPV/DMPOV in Monomers (Molar Ratio)	DDOPV/DMOPV in Polymer (Molar Ratio)	C_m (mole %)	Y_p (wt %)	$M_n \times 10^{-4}$	PDI	DP
DDOPV	PDDOPV	89	68	8.2	4.15	162
80/20	78.6/21.4	86	73	6.0	3.20	158
50/50	51.9/48.1	88	71	4.8	2.98	165
20/80	19.4/80.6	91	70	4.5	3.1	199
DMOPV	PDMOPV	87	70	—	—	—

DP, degree of polymerization.

680 cm^{-1}, corresponding to vibration of phenyl ring, ϕ—O—C, long alkyl, and C—Cl. The intensity of absorption peak for the dodecyloxy group increases with mol % content of DDOPV, using the intensity of absorption peak for phenyl ring at 1518 cm^{-1} as reference (Fig. 2).

Glass transition temperatures and decomposition temperature of the precursors of copolymer II from DSC analysis were listed in Table V. It can be noted that glass transition temperature of the long dodecyloxy groups (T_s) is located in the range of 70–75°C and seems to increase with decreasing DDOPV mol %. Glass transition temperature of the main chain (T_g) decreases with the increase of long alkoxy groups due to the interplasticization of the dodecyloxy groups as long soft side chains. Increase of the dodecyloxy group content also causes the decrease of decomposition temperature, because introduction of long side chains lowers the regularity and packing density of precursor copolymer **II**.

The precursors undergo elimination reaction at 140°C under vacuum for 6 h, and copolymer **II** with conjugated structure was obtained. IR spectrum of copolymer **II** shows the characteristic absorption of *trans* double bonds at 960 cm^{-1} and

Table V   DSC Data of Precursor Copolymer II [P(DMOPV-*co*-DDOPV)]

DDOPV/DMOPV (Molar Ratio)	T_s (°C)	T_g (°C)	T_d (°C)
PDDOPV	70	150	400
78.6/21.4	71	154	416
51.9/48.1	75	160	418
19.4/80.6	75	162	436
PDMOPV	—	—	453

that of C—H of olefin at 3010 cm^{-1}, as well as the disappearance of absorption peak for C—Cl after the elimination reaction. This fact demonstrates that the elimination reaction occurs completely.

Copolymer **II** is more soluble in chloroform than PPV or PDMOPV. Its solubility increases with DDOPV content. 95% of copolymer **II** containing 79 mol % DDOPV can be dissolved, whereas only 69% of copolymer **II** containing 52 mol % DDOPV can be dissolved.

Figure 3 illustrates the UV-visible spectra of copolymer **II** and PDDOPV films obtained by thermal elimination of the precursors. It is of interest to note that the spectrum of copolymer **II** is very similar to that of PDDOPV, whereas the spectrum of copolymer **I** is very similar to that of PPV.

The two random copolymers also show a difference in PL spectra. Wavelength of emitting peak for copolymer **I** changes with copolymer composition (Fig. 4), whereas that for copolymer **II** does not change with copolymer composition (Fig. 7). However, in both cases, the PL intensity increases with DDOPV content. Doi and coworkers[6] noted that, for the PL spectra of poly(2,5-dialkoxy-*p*-PV) with different alkoxy lengths, the positions of emitting peaks are the same, whereas the PL intensity increases with chain length of the alkoxy groups. No peak shift is probably due to the small difference in the electron-donating effect of different alkoxy groups. Enhancement of PL intensity with increase of DDOPV units may imply that the alkoxy groups reduce the ratio of nonradiative process due to preventing migration of excitons to traps.

The PL spectrum of the copolymer films is different from that of the copolymer in chloroform solution with regard to the wavelength of emitting
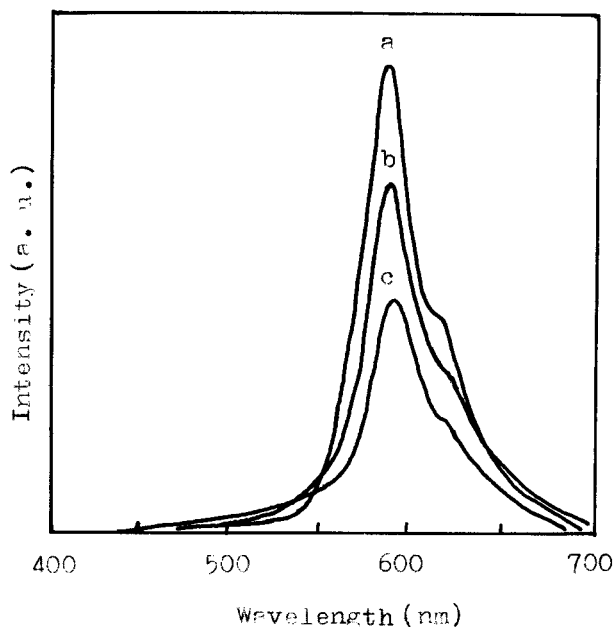
Figure 7   PL spectra of PDDOPV film (a), P(DMOPV-*co*-DDOPV) films containing 78.6 mole % DDOPV (b), and 51.9 mole % DDOPV (c).

peak (Table VI). The wavelength of the emitting peak in the PL spectrum of the film is larger than that in the solution. The reason may be that the energy transfer process takes place more easily in the film than in the solution and the excited state migrates to the emission center having smaller energy.

Table VII indicates the conductivity of copolymer **II** films doped by I_2 or $FeCl_3$. It can be noted that the conductivity of copolymer **II** film doped

Table VI   Wavelength of Emitting Peak in PL Spectra of the Two Random Copolymers in Film Form or in Solution

| Copolymer | DDOPV (mole %) | Wavelength (nm) | |
		Film	Solution
I	100	580	550
I	85.0	540	490
I	61.5	518	476
I	35.7	496	460
II	78.6	582	550
II	51.9	584	552
II	19.4	582	550
PPV	0	450	—
PDMOPV	0	580	—

Table VII   Conductivity of P(DMOPV-*co*-DDOPV) Doped with I_2 or $FeCl_3$

| DDOPV/DMOPV (Molar Ratio) | σ (S cm^{-1}) | |
	I_2	$FeCl_3$
PDDOPV	15.0	10.4
78.6/21.4	50.0	26
51.9/48.1	105	58
19.4/80.6	160	73
PDMOPV	190	86

by either I_2 or $FeCl_3$ increases with decreasing DDOPV content. This fact is probably due to the strong electron-donating effect of the methoxy group, compared with that of the dodecyl group. The conductivity of copolymer **II** is much higher than that of copolymer **I.**

CONCLUSIONS

Two kinds of random copolymers, P(PV-*co*-DDOPV) and P(DMOPV-*co*-DDOPV), were synthesized via the chlorine precursor route. The reactivity of DDOPV monomer is higher than that of the PV monomer, but is almost the same as that of DMOPV. The PDI of the precursor of P(PV-*co*-DDOPV) is higher than that of the precursor of P(DMOPV-*co*-DDOPV). T_g and T_d of the former precursor copolymer are higher than those of the latter precursor copolymer. UV-visible absorption spectra and PL spectra of P(PV-*co*-DDOPV) are quite different from those of P(DMOPV-*co*-DDOPV). Solubility of both kinds of random copolymers are better than that of PPV or PDMOPV. Conductivity of P(PV-*co*-DDOPV) is much lower than that of P(DMOPV-*co*-DDOPV). The alternating copolymer, P(PV-*alt*-DDOPV), was synthesized directly via the Heck coupling reaction and exhibited much higher molecular weight, lower PDI, and better solubility than those of the corresponding random copolymers. The UV-visible absorption spectrum of the alternating copolymer is different from that of the random copolymer with the near composition, but their PL spectra are very similar. The DSC curve of the alternating copolymer showed its liquid crystalline behavior.

REFERENCES

1. I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.,* **25,** 327 (1984).
2. Y. Park, E. Park, K. Kim, C. Park, and J. Jin, *Synth. Metal.,* **41,** 315 (1991).
3. J. L. Bredas, *Science,* **263,** 487 (1994).
4. D. Braun, A. J. Heeger, and H. Kroemer, *J. Electron. Mater.,* **20,** 945 (1991).
5. P. L. Burn, A. Kraft, D. R. Baigent, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, A. B. Holmes, and R. W. Jackson, *J. Am. Chem. Soc.,* **115,** 10117 (1993).
6. S. Doi, M. Kuwabara, T. Noguchi, and T. Ohnishi, *Synth. Metab.,* **55,** 4174 (1993).
7. N. N. Barashkov, D. J. Guerrero, H. J. Olivos, and J. P. Ferraris, *Synth. Metal.,* **75,** 153 (1995).
8. J. I. Jin, C. K. Park, and H. K. Shim, *Polymer,* **35,** 480 (1994).
9. R. W. Lenz, C. C. Han, and M. Lux, *Polymer,* **35,** 480 (1994).
10. A. Kraft, P. L. Burn, A. B. Holmes, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Synth. Metal.,* **55,** 936 (1993).
11. A. B. Holmes, D. D. C. Bradley, A. R. Brown, P. L. Burn, J. H. Burroughes, R. H. Friend, N. C. Greenham, R. W. Gymer, D. A. Halliday, R. W. Jackson, A. Kraft, J. H. F. Martens, K. Pichler, and I. D. W. Samuel, *Synth. Metal.,* **55,** 4031 (1993).
12. W. J. Swatos and B. Gorden, *Polym. Prepr.,* **31,** 505 (1990).
13. F. Wudl, S. Höger, C. Zhang, and A. J. Heeger, *Polym. Prepr.,* **34,** 179 (1993).
14. Z. Bao, Y. Chen, R. Cai, and L. Yu, *Macromolecules,* **26,** 5281 (1993).