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A Highly Selective Catalytic System for the Cross-Coupling of (*E*)-Styryl Bromide with Benzeneboronic Acid: Application to the Synthesis of All-Trans Poly(arylenevinylene)s

Masayuki Wakioka, Yuichiro Mutoh, Ryo Takita, and Fumiyuki Ozawa*

International Research Center for Elements Science (IRCELS), Institute for Chemical Research,
Kyoto University, Uji, Kyoto 611-0011

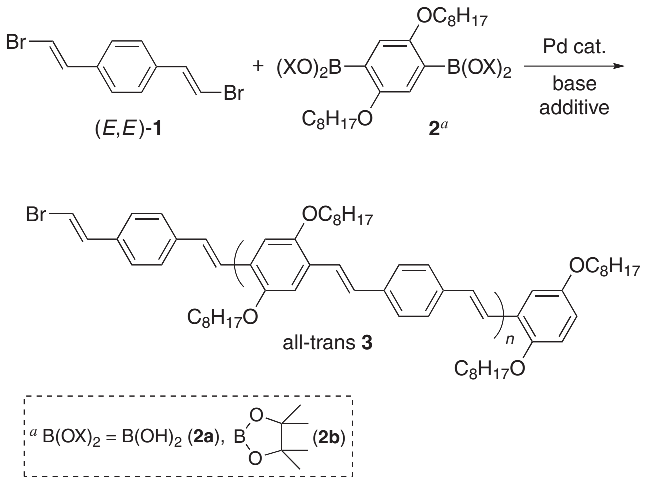
Received June 5, 2009; E-mail: ozawa@scl.kyoto-u.ac.jp

A highly selective system for palladium-catalyzed polycondensation of (*E*,*E*)-1,4-bis(2-bromoethenyl)benzene ((*E*,*E*)-**1**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2a**) to give all-trans poly[(*p*-phenylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] (all-trans **3**) has been investigated using (*E*)-styryl bromide ((*E*)-**4**) and 2,5-dioctyloxybenzeneboronic acid (**5a**) as model compounds of (*E*,*E*)-**1** and **2a**, respectively. The reaction of (*E*)-**4** and **5a** in toluene in the presence of $Pd(PPh_3)_4$ catalyst and aqueous K_2CO_3 base affords considerable amounts of homocoupling products (i.e., 1,4-diphenylbutadiene (13%) and 2,2′,5,5′-tetraoctyloxybiphenyl (22%)), together with (*E*)-2,5-dioctyloxystilbene ((*E*)-**6a**) as the cross-coupling product (30%). The use of aqueous NaOH as a strong base and Bu_4NBr as a phase-transfer catalyst notably reduces the homocoupling products, and the use of $Pd(PBu^t_3)_2$ instead of $Pd(PPh_3)_4$ results in almost perfect selectivity of the cross-coupling product (*E*)-**6a**. Under optimized catalytic conditions, the desired all-trans **3** has been successfully prepared without notable defects in the polymer chain.

Poly(phenylenevinylene)s (PPVs) and their homologs (i.e., poly(arylenevinylene)s: PAVs) are among the π-conjugated polymers that have wide application in optoelectronic devices such as light-emitting diodes (LEDs), photovoltaic cells, plastic lasers, and field-effect transistors (FETs).[1] It has been recognized that π-conjugated polymers are advantageous over small organic molecules as well as inorganic compounds in terms of accessibility of thin films by solution processes, which enable easy and low-cost fabrication of large-area devices. We have found that all-cis PPVs with the vinylene linkages entirely controlled to cis geometry exhibit a unique film-forming property.[2–4] Reflecting the all-cis geometry with a zigzag structure, the polymers are well soluble in common organic solvents and form highly amorphous films by spin-coating.[2,4] Furthermore, the resulting films become much less soluble under UV light, along with cis-to-trans isomerization of vinylene linkages to give all-trans PPVs.[2] On the basis of these findings, an extremely simple method of generating microscale patterns of all-trans PPVs on a quartz substrate has been developed. Given the fact that most of the devices have multilayer structures and the establishment of well-defined interfacial boundaries of thin films is of particular importance for gaining high device performance, this phenomenon (i.e., photoinduced insolubilization) should be useful for fabricating organic devices by solution processes.[5]

All-cis PPVs that form insoluble films of all-trans PPVs under UV light have been synthesized by palladium-catalyzed polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)benzene ((*Z*,*Z*)-**1**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2a**) (i.e., Suzuki–Miyaura-type polycondensation).[6] The resulting polymer bears 2-bromoethenyl and 2,5-dioctyloxybenzene groups, derived from (*Z*,*Z*)-**1** and **2a**, respectively, at each terminus.[3] It has been noted that the former group evidently facilitates the photoinduced insolubilization. Thus, although all-trans PPVs prepared by other synthetic methods are scarcely insolubilized under UV-irradiation,[7] all-trans PPVs prepared by Suzuki–Miyaura-type polycondensation (i.e., all-trans **3** in Scheme 1) possibly undergo photoinduced insolubilization. To examine this point, we attempted to prepare all-trans **3** under the same reaction conditions as applied for all-cis **3**.[3] However, as already documented for related systems,[9] unlike (*Z*,*Z*)-**1**, (*E*,*E*)-**1** was very prone to undergo homocoupling, and the resulting polymer contained structural defects including butadiene units in the main chain.

Therefore, we examined in this study highly selective conditions using (*E*)-styryl bromide ((*E*)-**4**) and 2,5-dioctyl-



Scheme 1.

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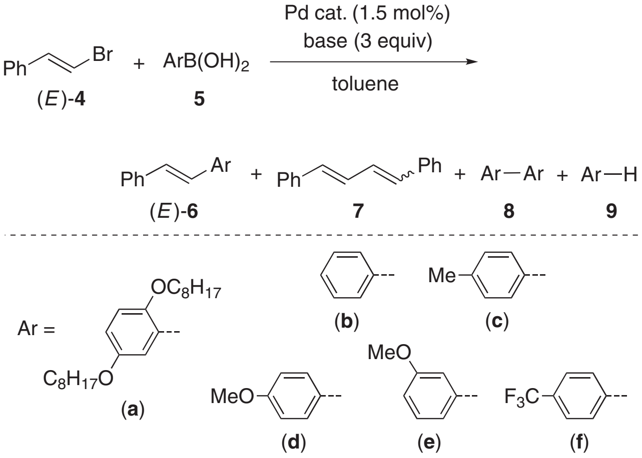
oxybenzeneboronic acid (**5a**) as model compounds of (*E*,*E*)-**1** and **2a**, respectively (Scheme 2). To our knowledge, Suzuki–Miyaura cross-coupling of (*E*)-styryl bromide has been limited to up to 90% yield,[10,11] while polycondensation requires almost perfect chemical yields.

Results and Discussion

Examination of Catalytic Conditions. Table 1 lists the results of cross-coupling of (*E*)-**4** with **5a** under various conditions. The reaction performed in toluene at 80 °C in the presence of $Pd(PPh_3)_4$ (1.5 mol %) and aqueous K_2CO_3 (3 equiv) afforded four kinds of products; i.e., cross-coupling product (*E*)-**6a** (30%), homocoupling products **7** (13%) and **8a** (22%), and a trace amount of 1,4-dioctyloxybenzene (**9a**) as a hydrolysis product of **5a** (Entry 1). Comparable results were obtained with Cs_2CO_3 and K_3PO_4 in place of K_2CO_3 (Entries 2 and 3). Thus, the highly reactive nature of (*E*)-**4** toward homocoupling has been evidenced.



Scheme 2.

Unlike previous reports,[9] Ag_2O did not improve the cross-coupling selectivity, but resulted in hydrolysis of **5a** (Entry 4). Metal fluorides[11c] were also ineffective (Entries 5 and 6). On the other hand, NaOH and KOH as strong bases notably enhanced the selectivity of (*E*)-**6a** (Entries 7 and 8). The selectivity was further improved by addition of Bu_4NBr and $(Octyl)_3MeNCl$ to the system (Entries 9–11). The combination of aqueous NaOH and Bu_4NBr was particularly effective, giving a quantitative yield of (*E*)-**6a** (Entry 9).

It is likely that the cross- and homocoupling reactions involve styrylpalladium of the formula *trans*-$Pd(CH{=}CHPh)Br(PPh_3)_2$ (**A**) as a common intermediate. In the cross-coupling, **A** reacts with **5a** via transmetallation to give $Pd(CH{=}CHPh)Ar(PPh_3)_2$, which reductively eliminates (*E*)-**6a**.[6] On the other hand, as we already confirmed for related *trans*-$Pd(CH{=}CHPh)Br(PMePh_2)_2$,[12] **A** also reacts with (*E*)-**4** via a novel homocoupling process induced by P–C reductive elimination.[13] Accordingly, **A** undergoes transmetallation and homocoupling competitively in the catalytic system. Since it is known that the association of areneboronic acid with a base is essential for transmetallation to take place,[7] it is reasonable that strong bases such as NaOH and KOH facilitate transmetallation. Furthermore, ammonium salts, which serve as a phase-transfer catalyst in a two-phase system consisting of toluene and water, enhance the efficiency of base, and thereby transmetallation rate.

Another approach to the highly selective cross-coupling system was accomplished with basic and bulky phosphine ligands, because we recently confirmed that the homocoupling reaction of (*E*)-**4** to give **7** is induced by P–C reductive

Table 1. Cross-Coupling Reaction of (*E*)-**4** and **5a**[a)]

Entry	Pd cat.	Base[b)]	Additive	Time/h	Yield/%[c)]			
					6a[d)]	**7**[e)]	**8a**	**9a**
1	$Pd(PPh_3)_4$	K_2CO_3	none	2	30 (97/3)	13 (29/71)	22	<1
2	$Pd(PPh_3)_4$	Cs_2CO_3	none	2	25 (99/1)	11 (18/82)	18	2
3	$Pd(PPh_3)_4$	K_3PO_4	none	2	31 (96/4)	11 (22/78)	20	<1
4	$Pd(PPh_3)_4$	Ag_2O	none	2	22 (98/2)	6 (77/23)	4	74
5	$Pd(PPh_3)_4$	KF	none	2	20 (98/2)	9 (28/72)	15	2
6	$Pd(PPh_3)_4$	CsF	none	2	21 (99/1)	10 (22/78)	16	2
7	$Pd(PPh_3)_4$	NaOH	none	2	95 (>99/1)	4 (42/58)	4	1
8	$Pd(PPh_3)_4$	KOH	none	2	72 (98/2)	27 (18/82)	20	4
9	$Pd(PPh_3)_4$	NaOH	Bu_4NBr	1	99 (>99/1)[h)]	0	<1	<1
10	$Pd(PPh_3)_4$	KOH	Bu_4NBr	1	97 (>99/1)	0	1	<1
11	$Pd(PPh_3)_4$	NaOH	Aliquat[f)]	1	97 (>99/1)	0	3	<1
12	$Pd(PCy_3)_2$	KOH	none	3	83 (99/1)	10 (16/84)	7	7
13	$Pd(PBu^t{}_3)_2$	NaOH	none	1	96 (>99/1)	<1	<1	2
14	$Pd(PBu^t{}_3)_2$	KOH	none	1	97 (>99/1)	<1	<1	2
15	$Pd(PBu^t{}_3)_2$	NaOH	Bu_4NBr	1	98 (>99/1)[i)]	0	<1	1
16[g)]	$Pd(PBu^t{}_3)_2$	NaOH	none	1	98 (>99/1)	0	<1	1
17[g)]	$Pd(PBu^t{}_3)_2$	KOH	none	1	98 (>99/1)	<1	<1	1
18[g)]	$Pd(PBu^t{}_3)_2$	K_2CO_3	none	8	55 (>99/1)	<1	1	<1

a) Unless otherwise noted, the reactions were run on a 0.20 mmol scale in toluene (1.0 mL) at 80 °C using Pd catalyst (3.0 µmol), base (0.60 mmol), and/or additive (0.20 mmol). b) Bases were employed as aqueous solutions (3.0 M). c) Determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard. d) E/Z ratios of **6a** are given in parentheses. e) E,E/E,Z ratios of **7** are given in parentheses. f) Aliquat 336: trioctylmethylammonium chloride. g) The reaction was run at room temperature. h) Isolated yield: 98%. i) Isolated yield: 97%.

elimination from **A**, and the P–C reductive elimination significantly decelerates when tertiary phosphines are highly basic and bulky.[13] As seen from Entries 12–18 in Table 1, PCy_3 was insufficient (Entry 12), but bulkier PBu^{t}_3 led to an almost quantitative yield of (*E*)-**6a** even in the absence of Bu_4NBr (Entries 13 and 14). The reaction successfully proceeded at room temperature (Entries 16–18). Interestingly, unlike the reaction using $Pd(PPh_3)_4$ (Entry 1), the homocoupling products were negligible even in the presence of K_2CO_3 (Entry 18).

The $Pd(PBu^{t}_3)_2$ catalyst was highly effective in the cross-coupling reactions of (*E*)-**4** with boronic acids with electron-rich aryl groups (**5b**–**5e** in Scheme 2), providing the desired (*E*)-**6** in nearly quantitative yields (Entries 1–4 in Table 2), while **5f** having an electron-deficient 4-trifluoromethylphenyl group formed a small amount of homocoupling product **7** (Entry 5). In these attempts, K_2CO_3 was found to be the base of choice; the boronic acids were hydrolyzed to a considerable extent in the presence of NaOH and KOH.

Synthesis and Characterization of All-Trans PAVs. All-trans **3** in Scheme 1 was synthesized under the catalytic conditions of Entry 9 in Table 1 (Entry 1 in Table 3). A 1:1 mixture of (*E*,*E*)-1,4-bis(2-bromoethenyl)benzene (**1**) and 2,5-dioctyloxybenzene-1,4-diboronic acid (**2a**) was heated in toluene at 80 °C for 24 h in the presence of $Pd(PPh_3)_4$ (1.5 mol %), aqueous NaOH (3 equiv), and Bu_4NBr (1 equiv), giving orange fluorescent suspension, which was diluted with CH_2Cl_2, washed with H_2O, and precipitated in methanol. The resulting polymer however contained diene structures in the main chain (ca. 5%) as confirmed by ^{1}H NMR spectroscopy. On the other hand, the reaction using $Pd(PBu^{t}_3)_2$ in place of $Pd(PPh_3)_4$ afforded all-trans **3** without notable defects in the PPV skeleton (Entry 2). The molecular weight decreased in the absence of Bu_4NBr (Entry 3), but increased when the reaction was carried out at room temperature using the pinacolate ester **2b** (Entry 4). The reaction was further improved in THF (Entry 5), and all-trans **3** with $M_n = 9700$ was obtained in a quantitative yield under a slightly warmed condition (Entry 6). Although the reaction was also examined under reflux conditions, the resulting polymer was insoluble in $CHCl_3$.

Table 2. Cross-Coupling Reactions of (*E*)-**4** and **5**[a)]

Entry	**5**	Time/h	Yield/%[b)]	
			6[c)]	**7**[d)]
1	**5b**	1	98 (>99/1)	<1
2	**5c**	1	98 (>99/1)	<1
3	**5d**	1	99 (>99/1)	<1
4	**5e**	2	97 (>99/1)	<1
5	**5f**	24	79 (>99/1)[e)]	5 (75/25)[e)]

a) All reactions were run on a 0.20 mmol scale in toluene (1.0 mL) at room temperature in the presence of $Pd(PBu^{t}_3)_2$ (3.0 µmol) and aqueous K_2CO_3 (3.0 M, 0.60 mmol). b) Isolated yields, unless otherwise noted. c) E/Z ratios of **6** determined by ^{1}H NMR spectroscopy are given in parentheses. d) E,E/E,Z ratios of **7** determined by ^{1}H NMR spectroscopy are given in parentheses. e) The product yields were determined by ^{1}H NMR analysis of the mixture of (*E*)-**6f** and **7** after chromatographic purification.

Polycondensation reactions of four kinds of (*E*,*E*)-bis(2-bromoethenyl)arenes (arene = *m*-phenylene (**10**), *o*-phenylene (**11**), 4,4′-biphenylene (**12**), and 2,7-fluorenylene (**13**)) with **2b** were also successful under the optimized conditions, giving the corresponding all-trans PAVs **14**–**17** without notable structural defects (Table 4).

The polymer structures were determined by NMR spectroscopy. Figure 1 compares the ^{1}H NMR spectrum of all-trans **3** (A) with that of 4-(2-bromoethenyl)stilbene (**18**) having the presumed terminal structures (B). The stereoregularity of vinylene linkages can be estimated from the peak intensities of the OCH_2 signals of octyloxy groups; the signal of *trans*-PPV appears at δ 4.08, whereas that of cis isomer at δ 3.54.[2,3] Thus, no trace of the signal of cis isomer was observed. Spectrum (A) exhibited the signals assignable to 2,5-dioctyloxyphenyl (a–d) and (*E*)-2-bromoethenyl (e) groups in reasonable intensities, showing the presence of these groups at the chain ends of all-trans **3**.

Finally, the performance in photoinduced insolubilization was investigated. A thin film of all-trans **3** ($M_n = 7500$, Entry 5 in Table 3) was prepared from a $CHCl_3$ solution (2.0 wt %) by spin-coating on a quartz substrate (i), irradiated with a Xe lamp ($\lambda = 300$–400 nm, 21.0 mW cm^{-2}) for 1 h under vacuum at room temperature (ii), and rinsed twice with $CHCl_3$ and dried (iii). The amount of thin-film on the quartz substrate at each step was evaluated by UV–vis spectroscopy.

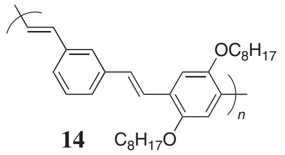
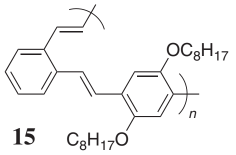
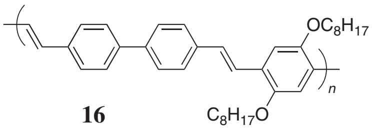
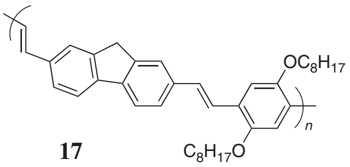
Figure 2 shows the UV–vis spectra. No notable change was observed before and after UV-irradiation ((i) and (ii)). On the other hand, the absorption intensity decreased to 22% after rinsing (iii). This remaining percent of film was clearly higher than that of all-trans PPV prepared by Hiyama-type polycondensation (8%),[7] but much lower than that of all-cis **3** (84%; $M_n = 7000$, $M_w/M_n = 2.69$).

Table 3. Polycondensation of (*E*,*E*)-**1** with **2**[a)]

Entry	Pd cat.	**2**	Bu_4NBr	Solvent	Temp/°C	Yield[b)]/%	M_n[c)]	M_w/M_n[c)]	cis/trans[d)]	Defect[d)]
1	$Pd(PPh_3)_4$	**2a**	1 equiv	toluene	80	>99	8400	3.03	<1/99	trace
2	$Pd(PBu^{t}_3)_2$	**2a**	1 equiv	toluene	80	>99	4900	2.48	<1/99	none
3	$Pd(PBu^{t}_3)_2$	**2a**	—	toluene	80	91	2700	1.57	<1/99	none
4	$Pd(PBu^{t}_3)_2$	**2b**	—	toluene	20	98	4100	1.44	<1/99	none
5	$Pd(PBu^{t}_3)_2$	**2b**	—	THF	20	>99	7500	1.80	<1/99	none
6	$Pd(PBu^{t}_3)_2$	**2b**	—	THF	30	>99	9700	1.96	<1/99	none

a) Reactions were carried out for 24 h using (*E*,*E*)-**1** (0.20 mmol), **2** (0.20 mmol), aqueous NaOH (3.0 M, 0.60 mmol), and Pd catalyst (3.0 µmol) in solution (2.0 mL). b) Yield of MeOH-insoluble polymer. c) Determined by GPC calibration based on polystyrene standards. d) Determined by ^{1}H NMR spectroscopy.

Table 4. All-Trans PAVs Prepared by Polycondensation of (*E*,*E*)-BrCH=CH–Ar–CH=CHBr **10**–**13** with **2b**[a)]

Entry	PAV	Yield/%[b)]	M_n[c)]	M_w/M_n[c)]	cis/trans[d)]
1	 **14**	>99	18300	2.10	<1/99
2	 **15**	99	9900	2.66	<1/99
3	 **16**	>99	7600	1.44	<1/99
4	 **17**	>99	6900	1.17	<1/99

a) Reactions were run at 20 °C for 24 h using (*E*,*E*)-**10**–**13** (0.20 mmol), **2b** (0.20 mmol), aqueous NaOH (3.0 M, 0.60 mmol), and $Pd(PBu^t_3)_2$ (3.0 μmol) in THF (2.0 mL). b) Yield of MeOH-insoluble polymer. c) Determined by GPC calibration based on polystyrene standards. d) Determined by ^{1}H NMR spectroscopy.

Conclusion

We found a highly selective catalytic system for Suzuki–Miyaura cross-coupling of (*E*)-styryl bromide ((*E*)-**4**) with areneboronic acids (**5**), giving almost quantitative yields of (*E*)-**6**. Under optimized conditions, five kinds of all-trans PAVs **3** and **14**–**17** were synthesized without notable structural defects in the polymer chain. Although all-trans **3** thus prepared underwent photoinduced insolubilization, its performance was much lower than that of all-cis **3**, showing the importance of all-cis configuration for photoinduced insolubilization.

Experimental

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz and ^{13}C NMR 100.62 MHz). Chemical shifts are reported in δ, referenced to the ^{1}H (residual protons) and ^{13}C signals of deuterated solvents. Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, and KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; $M_n = 980$–1920000). Melting points were measured with a Yanaco MP-S3 instrument. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PPV was performed with a Mikasa spin coater 1H-DX2. Photoirradiation was carried out at room temperature with an Asahi Spectra LAX-101 Xe lamp. UV–vis absorption spectra were recorded on a JASCO V-560 spectrometer.

Toluene (Kanto, dehydrated) and THF (Wako, dehydrated) were used as received. (*E*)-Styryl bromide ((*E*)-**4**) was purified under alkaline conditions to remove contamination of the Z isomer.[14] The following compounds were synthesized according to the literature: $Pd(PPh_3)_4$,[15] $Pd(PCy_3)_2$,[16] $Pd(PBu^t_3)_2$,[16] 2,5-dioctyloxybenzeneboronic acid (**5a**),[17] 2,5-dioctyloxy-1,4-benzenediboronic acid (**2a**),[18] and 2,5-dioctyloxy-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2b**).[3] All other chemicals, except for **8a** and (*E*,*E*)-**10**–**13** (see Supporting Information), were obtained from commercial suppliers and used without further purification.

Cross-Coupling of (*E*)-4 with 5a (Entry 9 in Table 1). A 10-mL Schlenk tube was charged with **5a** (75.7 mg, 0.200 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), Bu_4NBr (64.5 mg, 0.200 mmol), toluene (1 mL), and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). Compound (*E*)-**4** (36.6 mg, 0.200 mmol) was added, and the mixture was stirred at 80 °C for 1 h. After cooling to room temperature, the mixture was passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), concentrated to dryness, and examined by ^{1}H NMR using hexamethylbenzene as an internal standard, showing the formation of (*E*)-2,5-dioctyloxystilbene (**6a**, E/Z > 99/1) in 99% yield, which was isolated as a colorless oil by column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (4/1)) (85.7 mg, 98% yield). The NMR data for (*E*)-**6a** were identical to those reported.[19] ^{1}H NMR ($CDCl_3$): δ 7.52 (d, $J = 7.5$ Hz, 2H, $H^{2,6}$ of C_6H_5), 7.46 (d, $J = 16.5$ Hz, 1H, $C_6H_3CH{=}CH$), 7.35 (t, $J = 7.7$ Hz, 2H, $H^{3,5}$ of C_6H_5), 7.24 (t, $J = 7.5$ Hz, 1H, H^4 of C_6H_5), 7.15 (d, $J = 3.0$ Hz, 1H, H^6 of C_6H_3), 7.11 (d, $J = 16.5$ Hz, 1H, $C_6H_3CH{=}CH$), 6.82 (d, $J = 8.9$ Hz, 1H, H^3 of C_6H_3), 6.77 (dd, $J = 8.9$, 2.9 Hz, 1H, H^4 of C_6H_3), 3.96 (t, $J = 6.5$ Hz, 2H, OCH_2), 3.95 (t, $J = 6.5$ Hz, 2H, OCH_2), 1.87–1.73 (m, 4H, CH_2), 1.54–1.23 (m, 20H, CH_2), 0.93–0.84 (m, 6H, CH_3).

Cross-Coupling of (*E*)-4 with 5b–5f. A typical procedure is reported for Entry 2 in Table 2. A 10-mL Schlenk tube was

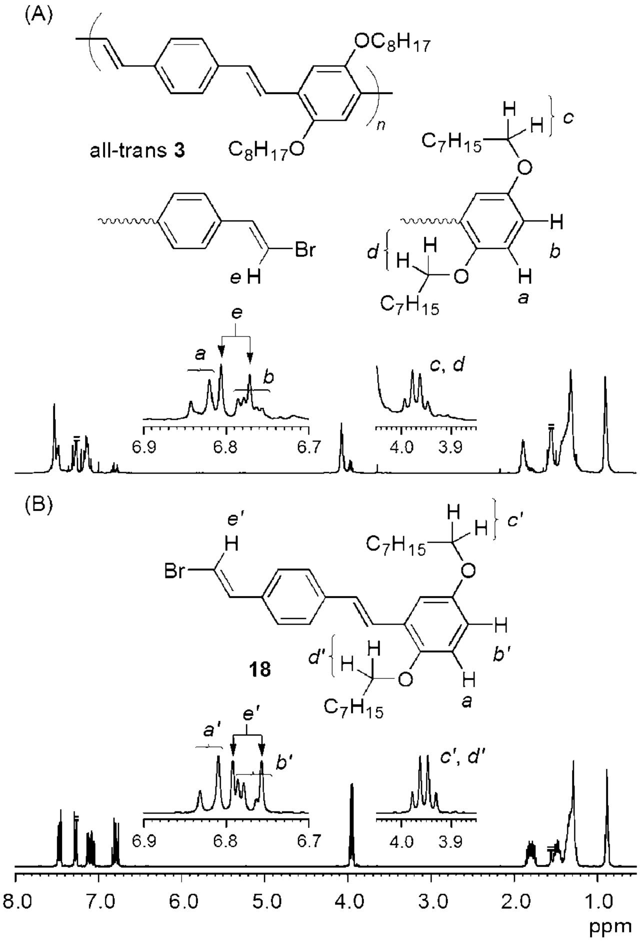


Figure 1. ^{1}H NMR spectra of (A) all-trans **3** (Run 2 in Table 2) and (B) 4-(2-bromoethenyl)stilbene (**18**) in $CDCl_3$ at room temperature.

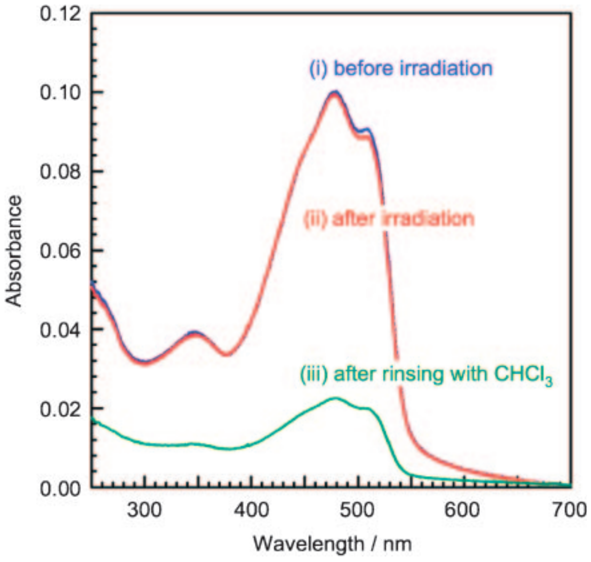


Figure 2. UV–vis absorption spectra of all-trans **3** (M_n = 7500) in thin film, before and after UV-irradiation (i and ii), and after rinsing twice with $CHCl_3$ (iii).

charged with **5b** (24.4 mg, 0.200 mmol), $Pd(PBu^t_3)_2$ (1.5 mg, 3.0 µmol), toluene (1 mL), and 3.0 M aqueous K_2CO_3 (0.20 mL, 0.60 mmol). Compound (*E*)-**4** (36.6 mg, 0.200 mmol) was added, and the mixture was stirred at room temperature for 1 h. The mixture was passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), concentrated to dryness, and examined by ^{1}H NMR, showing the absence of butadiene **7**. Purification by column chromatography (SiO_2, hexane) afforded (*E*)-**6b** as a white solid (35.3 mg, 98% yield). The NMR data of (*E*)-**6b**–**6f** were identical to those reported.[20]

(*E*)-6b:[20a] ^{1}H NMR ($CDCl_3$): δ 7.51 (d, J = 7.3 Hz, 4H, C_6H_5), 7.35 (t, J = 7.4 Hz, 4H, C_6H_5), 7.25 (t, J = 7.2 Hz, 2H, C_6H_5), 7.10 (s, 2H, CH=CH).

(*E*)-6c:[20b] ^{1}H NMR ($CDCl_3$): δ 7.49 (d, J = 7.3 Hz, 2H, C_6H_5), 7.40 (d, J = 8.0 Hz, 2H, C_6H_4), 7.34 (t, J = 7.7 Hz, 2H, C_6H_5), 7.23 (t, J = 7.7 Hz, 1H, C_6H_5), 6.15 (d, J = 8.0 Hz, 2H, C_6H_4), 7.09 and 7.04 (each d, J = 16.6 Hz, 2H, CH=CH), 2.35 (s, 3H, CH_3).

(*E*)-6d:[20b] ^{1}H NMR ($CDCl_3$): δ 7.47 (d, J = 7.3 Hz, 2H, C_6H_5), 7.44 (d, J = 8.7 Hz, 2H, C_6H_4), 7.33 (t, J = 7.5 Hz, 2H, C_6H_5), 7.22 (t, J = 7.4 Hz, 1H, C_6H_5), 7.06 and 6.96 (each d, J = 16.3 Hz, 2H, CH=CH), 6.88 (d, J = 8.7 Hz, 2H, C_6H_4), 3.80 (s, 3H, OCH_3).

(*E*)-6e:[20b] ^{1}H NMR ($CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 2H, C_6H_5), 7.34 (t, J = 7.4 Hz, 2H, C_6H_5), 7.29–7.21 (m, 2H, C_6H_5 and C_6H_4), 7.10 (d, J = 16.4 Hz, 1H, CH=CH), 7.10 (d, J = 7.7 Hz, 1H, C_6H_4), 7.06 (d, J = 16.4 Hz, 1H, CH=CH), 7.04 (t, J = 1.8 Hz, 1H, C_6H_4), 6.81 (dd, J = 8.2, 2.4 Hz, 1H, C_6H_4), 3.83 (s, 3H, OCH_3).

(*E*)-6f:[20c] ^{1}H NMR ($CDCl_3$): δ 7.62–7.55 (m, 4H, C_6H_4), 7.52 (d, J = 7.3 Hz, 2H, C_6H_5), 7.37 (t, J = 7.2 Hz, 2H, C_6H_5), 7.29 (t, J = 7.2 Hz, 1H, C_6H_5), 7.18 and 7.10 (each d, J = 16.4 Hz, 2H, CH=CH).

Synthesis of All-Trans PPV (3). A 10-mL Schlenk tube was charged with (*E*,*E*)-**1** (57.6 mg, 0.200 mmol), **2a** (84.4 mg, 0.200 mmol), Bu_4NBr (64.5 mg, 0.200 mmol), toluene (2 mL), and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). The complex $Pd(PBu^t_3)_2$ (1.5 mg, 3.0 µmol) was added, and the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (5 mL), washed with water, and then poured into a vigorously stirred MeOH (50 mL). An orange precipitate of all-trans **3** was collected by membrane filter (0.5 µm), washed with MeOH, and dried under vacuum at room temperature overnight (94.4 mg, >99% yield). ^{1}H NMR ($CDCl_3$): δ 7.53 (s, C_6H_4), 7.50 (d, J = 16.5 Hz, CH=CH), 7.50–7.45 (m, $H^{2,6}$ of terminal $C_6H_4CH{=}CHBr$), 7.30 (d, J = 8.6 Hz, $H^{3,5}$ of terminal $C_6H_4CH{=}CHBr$), 7.15 (d, J = 16.7 Hz, CH=CH), 7.14 (s, $H^{3,6}$ of C_6H_2), 7.11 (d, J = 14.2 Hz, C*H*=CHBr of terminal $C_6H_4CH{=}CHBr$), 6.83 (d, J = 9.1 Hz, H^3 of terminal $C_6H_3(OC_8H_{17})_2$), 6.79 (d, J = 14.0 Hz, 1H, CH=C*H*Br), 6.77 (dd, J = 8.9, 2.8 Hz, H^4 of terminal $C_6H_3(OC_8H_{17})_2$), 4.08 (t, J = 6.0 Hz, OCH_2), 3.98 and 3.96 (t, J = 6.3 Hz, OCH_2 of terminal $C_6H_3(OC_8H_{17})_2$), 1.96–1.80 and 1.62–1.18 (m, CH_2), 0.94–0.80 (m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 137.2 (s, $C^{1,4}$ of C_6H_4), 128.5 (s, CH=CH), 127.0 (s, $C^{1,2}$ of C_6H_2), 126.8 (s, $C^{2,3,5,6}$ of C_6H_4), 123.2 (s, CH=CH), 110.6 (s, $C^{3,6}$ of C_6H_2), 69.6 (s, OCH_2), 31.8, 29.5, 29.4, 29.3, 26.3, 22.7 (each s, CH_2), 14.1 (s, CH_3).

Synthesis of All-Trans PAVs (14–17). These polymers were synthesized similarly to all-trans **3** using (*E*,*E*)-**10**–**13** (0.200 mmol), **2b** (117 mg, 0.200 mmol), THF (2 mL), 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol), and $Pd(PBu^t_3)_2$ (1.5 mg, 3.0 µmol) at 20 °C for 24 h.

All-Trans 14: Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.65 (s, H^2 of C_6H_4), 7.54 (d, $J = 16.3$ Hz, CH=CH), 7.48 (d, $J = 7.5$ Hz, $H^{4,6}$ of C_6H_4), 7.38 (t, $J = 7.3$ Hz, H^5 of C_6H_4), 7.22–7.13 (m, $H^{3,6}$ of C_6H_2 and CH=CH), 4.10 (t, $J = 6.0$ Hz, OCH_2), 1.96–1.83 and 1.63–1.18 (m, CH_2), 0.92–0.80 (m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 138.3 (s, $C^{1,3}$ of C_6H_4), 128.9 (s, CH=CH), 127.0 (s, $C^{1,2}$ of C_6H_2), 125.5 and 125.3 (each s, C^2 and C^6 of C_6H_4), 123.8 (s, CH=CH), 110.9 (s, $C^{3,6}$ of C_6H_2), 69.7 (s, OCH_2), 31.8, 29.5, 29.4, 29.4, 26.3, and 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-Trans 15: Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.70–7.58 (m, C_6H_4), 7.53 (d, $J = 16.2$ Hz, CH=CH), 7.37 (d, $J = 16.2$ Hz, CH=CH), 7.32–7.22 (m, C_6H_4), 7.12 (s, $H^{3,6}$ of C_6H_2), 3.99 (t, $J = 6.3$ Hz, OCH_2), 1.83–1.68 and 1.50–1.12 (m, CH_2), 0.90–0.77 (m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 136.7 (s, $C^{1,2}$ of C_6H_4), 127.5 (s, CH=CH), 127.2 (s, $C^{1,4}$ of C_6H_2), 126.9, 126.8, and 126.1 (each s, $C^{3,6}$ and $C^{4,5}$ of C_6H_4 and CH=CH), 110.8 (s, $C^{3,6}$ of C_6H_2), 69.5 (s, OCH_2), 31.8, 29.5, 29.4, 29.4, 26.3, and 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-Trans 16: Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.70–7.48 (m, C_6H_4), 7.55 (d, $J = 16.3$ Hz, CH=CH), 7.19 (d, $J = 16.3$ Hz, CH=CH), 7.17 (s, $H^{3,6}$ of C_6H_2), 4.09 (t, $J = 6.3$ Hz, OCH_2), 1.96–1.80 and 1.63–1.18 (m, CH_2), 0.94–0.82 (m, CH_3). $^{13}C\{^1H\}$ NMR analysis was not feasible due to low solubility.

All-Trans 17: Orange solid. ^{1}H NMR ($CDCl_3$): δ 7.83–7.68 and 7.62–7.46 (m, Fl), 7.55 (d, $J = 16.0$ Hz, CH=CH), 7.24–7.10 (m, $H^{3,6}$ of C_6H_2 and CH=CH), 4.10 (t, $J = 6.3$ Hz, OCH_2), 1.97–1.81 and 1.65–1.18 (m, CH_2), 0.96–0.82 (m, CH_3). $^{13}C\{^1H\}$ NMR analysis was not feasible due to low solubility.

Synthesis of (*E*,*E*)-4′-(2-Bromoethenyl)-2,5-dioctyloxystilbene (18). To a solution of (*E*,*E*)-**1** (130 mg, 0.450 mmol) and **5a** (114 mg, 0.300 mmol) in toluene (1.5 mL) were successively added $Pd(PBu^t_3)_2$ (2.3 mg, 4.5 µmol) and 3.0 M aqueous KOH (0.30 mL, 0.90 mmol). The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), and purified by flash column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (10/1)), giving the title compound as a yellow solid (89.2 mg, 55% yield). Mp: 44–46 °C. ^{1}H NMR ($CDCl_3$): δ 7.47 (d, $J = 16.3$ Hz, 1H, $C_6H_3C\mathit{H}{=}CH$), 7.46 (d, $J = 8.3$ Hz, 2H, $H^{2',6'}$ of C_6H_4), 7.28 (d, $J = 8.2$ Hz, 2H, $H^{3',5'}$ of C_6H_4), 7.13 (d, $J = 3.7$ Hz, 1H, H^6 of C_6H_3), 7.10 (d, $J = 14.0$ Hz, 1H, $C\mathit{H}{=}CHBr$), 7.07 (d, $J = 16.5$ Hz, 1H, $C_6H_3CH{=}C\mathit{H}$), 6.83 (d, $J = 8.9$ Hz, 1H, H^3 of C_6H_3), 6.78 (d, $J = 13.9$ Hz, 1H, $CH{=}C\mathit{H}Br$), 6.78 (dd, $J = 9.1$, 2.8 Hz, 1H, H^4 of C_6H_3), 3.96 (t, $J = 6.3$ Hz, 2H, OCH_2), 3.95 (t, $J = 6.4$ Hz, 2H, OCH_2), 1.87–1.73 (m, 4H, CH_2), 1.54–1.23 (m, 20H, CH_2), 0.93–0.85 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.3 and 151.0 (each s, $C^{2,5}$ of C_6H_3), 138.0 and 134.8 (each s, $C^{1',4'}$ of C_6H_4), 136.9 (s, $\mathit{C}H{=}CHBr$), 128.3 (s, CH=CH), 127.3 (s, C^1 of C_6H_3), 126.9 and 126.4 (each s, $C^{2',3',5',6'}$ of C_6H_4), 124.1 (s, CH=CH), 114.7, 113.9, and 112.3 (each s, $C^{3,4,6}$ of C_6H_3), 106.2 (s, $CH{=}\mathit{C}HBr$), 69.5 and 68.7 (each s, OCH_2), 31.8, 31.8, 29.5, 29.4, 29.4, 29.3, 29.3, 26.3, 26.3, 26.1, and 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd for $C_{32}H_{45}BrO_2$: C, 70.96; H, 8.37%. Found: C, 70.81; H, 8.45%.

Photoinduced Insolubilization of PPV. A solution of PPV in $CHCl_3$ (2.0 wt %) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 µm, Hydrophobic; ADVANTEC). A thin-film of PPV was prepared by spin-coating on a quartz plate (1 cm^2); the filtrate (50 µL) was added dropwise on a plate, and the plate was accelerated to 1200 rpm for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. After drying under vacuum at room temperature for 30 min, the film was placed in a quartz cell under N_2 atmosphere, and analyzed by UV–vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, and irradiated by a Xe lamp ($\lambda_{max} = 365$ nm, 21.0 mW cm^{-2}) for 60 min under vacuum at room temperature. UV–vis absorption spectrum of the resulting film was then recorded. The film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum at room temperature, and examined by UV–vis absorption spectroscopy.

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Supporting Information

Experimental procedures for the preparation of **8a** and (*E*,*E*)-**10**–**13**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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