Synthesis and Photochemical Properties of Poly(phenylenevinylene)s with Highly Regulated Structures

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General Introduction

Background

Photo-induced Insolubilization of PPVs. \(\pi\)-Conjugated polymers such as poly-(phenylenevinylene)s (PPVs), poly(phenyleneethynylene)s (PPEs), poly(phenylene)s (PPs), and poly(thienylene)s (PTs) have been studied extensively as organic semiconductive materials because of their desirable electronic, optical, and mechanical properties (Chart 1).\(^1,2\) These polymers have found wide application in electronic and optoelectronic devices including light-emitting diodes (LEDs), photovoltaic cells, plastic lasers, and field-effect transistors (FETs). It has been recognized that \(\pi\)-conjugated polymers are advantageous over small organic molecules as well as inorganic compounds in terms of accessibility and flexibility of thin films. Accordingly, the polymers must be soluble so as to fabricate devices using easy and low-cost techniques based on wet processes. However, \(\pi\)-conjugated polymers often have a rigid framework and are hardly soluble in common organic solvents. Therefore, considerable efforts have been devoted to improving the solubility and processability. The incorporation of relatively long and flexible side chains such as alkyl and alkoxy groups onto the polymer backbone is a common method to prepare soluble polymers.

On the other hand, the solubility is often obstructive to the application of \(\pi\)-conjugated polymers. Since it is difficult to gain high device performance with a single component, several kinds of polymers are commonly combined in layers by wet processes. It has been known that the establishment of well-defined interfacial boundary of thin films is of particular importance to achieve high performance of multilayered devices.\(^3\) Several approaches to
insolubilizing thin films have been developed to avoid the mixing of polymer layers within the interface. One is the selection of an appropriate solvent for each step, and the other is the use of the polymers containing photo- or thermal-cross-linkable functional groups. However, in any cases, the design and synthesis of appropriate polymers are not so easy task, and therefore more simple and efficient ways of insolubilizing films are desirable.

The author’s group has recently found that PPVs bear very interesting properties when the vinylene linkages are entirely regulated to cis geometry. Thus, reflecting the all-cis configuration with a zigzag structure, all-cis poly(p-phenylenevinylene)s (PpPVs) (1, eq 1) are highly soluble in common organic solvents, and exhibit excellent film-forming properties to provide highly amorphous films. Furthermore, the resulting films are insolubilized under UV-irradiation, along with cis-to-trans isomerization of PpPVs. The photo-induced insolubilization has been successfully applied to direct microscale patterning of PpPVs onto quartz substrates.

This phenomenon is unique to all-cis PpPVs (1) prepared by Suzuki–Miyaura-type polycondensation of (Z,Z)-1,4-bis(2-bromoethenyl)benzene (2) and 2,5-dioctyloxy-1,4-benzenediboronic acid (3) (eq 2). For example, all-trans isomers (6) independently prepared by Hiyama-type polycondensation of (E,E)-1,4-bis(2-silylthienyl)benzene (4) and 2,5-dioctyloxy-1,4-diodobenzene (5) (eq 3) and poly(2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as a commercial product are scarcely insolubilized by UV-irradiation.
Since the above method of insolubilizing thin films is extremely simple, and possibly applied to other \( \pi \)-conjugated polymers, the author has been interested in elucidation of the factors governing the insolubilization phenomenon. Although photoisomerization appears to serve as a key factor, there is a possibility that several structural features characteristic of all-cis PPVs cause the insolubilization synergistically.

**One-way Photoisomerization of PPVs.** Alkenes are generally converted to a mixture of cis and trans isomers in the photostationary state, as typically documented for stilbene (7) (Scheme 1A).\(^\text{17}\) This mutual conversion process is referred to as “two-way photoisomerization”. On the other hand, some kinds of alkene with an extended \( \pi \)-conjugated system undergo “one-way photoisomerization”, solely from cis to trans isomers, through a
quantum chain process involving triplet excited states (Scheme 1B). 1-(2-Anthryl)-2-phenylethene (8) is among the representative examples. All-cis PpPVs follow the same isomerization process, as evidenced by the studies using all-cis and all-trans oligo(ρ-phenylvinylene)s (OpPVs) as well-defined models of PpPVs (Scheme 2). It has been found that the isomerization mechanism changes from two-way to one-way, with extension of the π-conjugation lengths from OpPV-1 to OpPV-2.

Scheme 1

(A) two-way photoisomerization

(B) one-way photoisomerization

Terminal Structures of All-cis PPVs. Besides the all-cis configuration, PpPVs (1) prepared by Suzuki–Miyaura-type polycondensation have a characteristic structural feature; i.e., they are mainly composed of the polymer bearing 4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus (1x, Chart 2). Indeed, 1x reacts with 2,5-dioctyloxybenzeneboronic acid in the presence of a palladium catalyst to give 1y bearing 2,5-dioctyloxyphenyl groups at both ends. Since the terminal groups of all-cis 1x are very probably preserved in all-trans PpPV formed by photoisomerization, but not in all-trans PpPV (6) prepared by Hiyama-type polycondensation (eq 3), there is a possibility that the unique terminal structure of 1x serves as a promoter of the photo-induced insolubilization.
Scheme 2

\[ \text{cis-OpPV-1} \xrightarrow{\text{hv}} \text{trans-OpPV-1} \quad \text{two-way} \]
\[ \text{cis-OpPV-2-4} \xrightarrow{\text{hv}} \text{trans-OpPV-2-4} \quad \text{one-way} \]

Chart 2

all-cis PpPV (1x)

all-cis PpPV (1y)
**General Introduction**

**On the Factors for Photo-induced Insolubilization.** Taking the above observations into account, the author set about the following subjects.

1. Effect of all-cis and all-trans configurations on photo-induced insolubilization.
2. Effect of terminal structures on photo-induced insolubilization.
3. Effect of molecular weight on photo-induced insolubilization.
4. Effect of \( \pi \)-conjugation length on photoisomerization in polymer systems.

To deal with these subjects, the following sets of PPVs with all-cis and all-trans configurations have been required in a range of molecular weights, respectively (Chart 3). Among them, all-cis PpPVs (1x and 1y) have already been synthesized, whereas all-trans PpPVs (1x) bearing the same terminal groups as all-cis 1x and all-cis and all-trans poly(m-phenylenevinylene)s (PmPVs, 9a–c) bearing relatively short effective \( \pi \)-conjugation lengths interrupted by \( m \)-phenylene units have not been obtained. The all-cis and all-trans

![Chart 3](image-url)
isomers of 9a–c may be prepared similarly to all-cis 1 and all-trans 6, respectively. On the other hand, although all-trans 1x having 4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl groups at each terminus needs to be prepared by Suzuki–Miyaura-type polycondensation, the previous attempts in this group have been unsuccessful due to contamination of the polymer chain with butadiene and biaryl units (eq 4).

These structural defects are due to homo-coupling processes. Because structural defects once generated in the polymer chain are unable to be removed by purification, the establishment of a highly selective catalytic condition has been essential to achieve the synthesis of all-trans PpPVs.

**Cross-Coupling vs. Homo-Coupling Reactions.** Cross-coupling reactions of alkenyl halides with organometallic reagents are useful means of regio- and stereo-selective synthesis of alkenes. However, they often involve undesirable homo-coupling reactions. For example, Negishi coupling of alkenyl iodide (10) with methylzinc chloride catalyzed by [Pd(PPh₃)₄] forms butadiene 12 as the homo-coupling product, together with 11 as the cross-coupling product (eq 5).
Scheme 3 illustrates the catalytic cycle of cross-coupling generally accepted. First, a low-valent palladium species $\text{[Pd(PR}_3\text{)]}_2$ undergoes oxidative addition of alkenyl halides to form an alkenylpalladium intermediate $\text{A}$. Transmetalation of $\text{A}$ with organometallic compounds affords intermediate $\text{B}$, which reductively eliminates cross-coupling products, along with regeneration of $\text{[Pd(PR}_3\text{)]}_2$. Mechanistic studies using experimental and computational techniques have shown that transmetalation serves as the rate-determining step in many catalytic systems.$^{21}$ Consequently, it is likely that the homo-coupling reaction proceeds from $\text{A}$ as a common intermediate.
In contrast to the extensive studies of cross-coupling reactions, the mechanism of homo-coupling reactions has been little explored.\textsuperscript{23–25} Scheme 4 illustrates a schematic view of homo-coupling processes so far reported. Organopalladium intermediate A’, formed by oxidative addition of organic halide (R–X) to a low-valent palladium species (step a), possibly undergoes two reaction processes (A and B). Process A involves disproportionation of A’ to give diorgano (C) and dihalogeno (D) complexes (step b), and C subsequently undergoes reductive elimination of homo-coupling product (R–R) (step c).\textsuperscript{24} On the other hand, process B involves oxidative addition of R–X to an anionic species (E), generated by chemical or electrochemical reduction of A’ (step d → step e). The resulting diorganopalladium C reductively eliminates R–R (step f).\textsuperscript{25} The reaction mechanism possibly depends on catalytic conditions including the sorts of organic halides and supporting ligands. For example, process A has been proposed for the homo-coupling reaction of aryl halides catalyzed by a Pd/bipy complex,\textsuperscript{24} while process B for the reaction of aryl triflates promoted by a Pd/PPh\textsubscript{3} catalyst.\textsuperscript{25} In any case, however, the mechanistic information is extremely limited, and direct information about the present catalytic systems of all-trans PpPV synthesis is desirable.
Outline of the Thesis

To elucidate the unique photochemical properties of all-cis PpPVs, the author deals with the subjects (1)–(4) set in the previous section by examining the following topics.

Chapter 1 deals with photo-induced insolubilization of all-cis PpPVs (1) (subjects (2) and (3)) (eq 6). To investigate the effects of terminal structures and molecular weights on photo-induced insolubilization, the author prepared all-cis 1x and 1y (Chart 3) with a range of molecular weights, and examined their performance by a quantitative method using UV-vis absorption spectroscopy. It has been found that the performance of all-cis PpPVs on photo-induced insolubilization is significantly affected by terminal structures as well as molecular weights; namely, 2-bromoethenyl groups at the polymer end facilitates the insolubilization to a notable extent.

![Diagram](6)

Chapter 2 deals with photoisomerization of PPVs (subject (4)). To examine the effects of \( \pi \)-conjugation lengths on photoisomerization, all-cis and all-trans PmPVs (9a–c) having relatively short effective \( \pi \)-conjugation lengths (Chart 3) were synthesized in almost perfect stereoregularities by Suzuki–Miyaura-type and Hiyama-type polycondensation, respectively. It has been found that the resulting PmPVs undergo two-way photoisomerization both in solution and thin films, in contrast to PpPVs, which undergo one-way photoisomerization (Scheme 5). Thus, the dependence of the photoisomerization mechanism on \( \pi \)-conjugation lengths has been clarified for the first time in polymer systems.
To examine whether the all-cis configuration of PpPVs is essential or not on photo-induced insolubilization (subject (1)), all-trans PpPVs bearing a 2-bromoethenyl group (all-trans 1x, Chart 3) has been required. For ensuring the highly selective synthesis of all-trans PpPVs without structural defects, the author has examined in Chapter 3 to clarify the mechanism of homo-coupling giving 1,4-diphenylbutadiene from styryl bromide. Thus, the isolated *trans*-\(\text{[Pd(\text{CH}=\text{CHPh})\text{Br(PMePh}_2\text{)}_2]}\) (13) as a model of presumed intermediate was treated with (\(E\))-styryl bromide (14) in a stoichiometric system, and the reaction was investigated in detail by NMR spectroscopy and kinetic techniques. The study has revealed that \([\text{Pd}(\eta^2-(\text{E})-\text{PhCH}=\text{CHPhMe})\text{Br(PMePh}_2\text{)}_2]\) (15) formed by P–C reductive elimination from (\(E\))-13 catalyzes the conversion of (\(E\))-13 and (\(E\))-14 into *trans*-\(\text{[PdBr}_2\text{(PMePh}_2\text{)}_2}\) (16) and 1,4-diphenylbutadiene (17) (Scheme 6).
In this connection, Chapter 4 deals with the mechanism of \( \text{P–C reductive elimination} \) from trans-\([\text{Pd}(\text{CH}=\text{CHPh})\text{Br(PMePh}_2)_2]\) (13) to afford \([\text{Pd}(\eta^2\text{-PhCH}=\text{CHMePh}_2)\text{Br-(PMePh}_2)]\) (15) and \([\text{Pd}(\eta^2\text{-PhCH}=\text{CHMePh}_2)(\text{PMePh}_2)_2]\text{Br (18)}\) (Scheme 7). It has been shown that the P–C reductive elimination is strongly dependent on E/Z configurations of styryl ligand. Thus, the \((E)\)-isomer of 13 easily undergoes P–C reductive elimination. On the other hand, while the \((Z)\)-isomer of 13 is inactive toward P–C reductive elimination, the \((Z)\)-styrylphosphonium complex \((Z)-15\) undergoes P–C oxidative addition to give \((Z)-13\). Kinetic examinations clearly demonstrate that the P–C reductive elimination from \((E)-13\) proceeds via either a dissociative or an associative path, depending on the amount of free PMePh\(_2\) in the system.

**Scheme 7.**

Chapter 5 describes highly selective synthesis of all-trans PpPVs (1x) via Suzuki–Miyaura-type polycondensation (eq 7). The catalytic conditions were investigated for a model reaction of \((E)\)-styryl bromide with 2,5-dioctyloxybenzenephosphonic acid, taking the mechanistic information gained in Chapters 3 and 4 into consideration. The combination of \([\text{Pd(PBu}_3)_2]\), aqueous NaOH, and \(\text{Bu}_4\text{NBr} \) was found to be particularly effective for cross-coupling, and thereby all-trans PpPVs without structural defects were successfully prepared by polycondensation of \((E,E)-2\) with 3. A detailed NMR analysis of the resulting all-trans PpPVs revealed the same terminal structures as found in all-cis PpPVs. The polymers did undergo photo-induced insolubilization in thin films, but their performance was
much lower than that of all-cis isomers. Hence, the importance of all-cis configuration of PpPVs for the photo-induced insolubilization has been evidenced.

\[
\text{(E,E)-2} \quad \overset{[\text{Pd(PBu}_3]_2]}{\text{aq NaOH}} \quad \overset{\text{Bu}_4\text{NBr}}{\text{3}} \quad \overset{\text{all-trans PpPV (1)}}{\text{O}}
\]

References and Notes


(b) Miyaura N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 2.  
(c) Hiyama T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J. Eds; WILEY-VCH, Weinheim, Germany, 1998; Chapter 10.  
(d) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 4.  
General Introduction


Chapter 1

Effects of Primary Structures on Photo-induced Insolubilization of Poly(phenylenevinylene)s in Thin Films

Abstract

All-cis poly(ρ-phenylenevinylene)s (PpPVs) prepared by Suzuki–Miyaura-type polycondensation of (Z,Z)-1,4-bis(2-bromoethyl)benzene with 2,5-dioctyloxybenzene-1,4-diboronic acid undergo photo-induced insolubilization in thin films, along with trans-to-cis isomerization of vinylene groups to give all-trans PpPVs. This phenomenon has been investigated with two types of all-cis PpPVs having different terminal structures; one bears (Z)-4-(2-bromoethyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus, whereas the other has 2,5-dioctyloxyphenyl groups at both ends. The amount of all-trans PpPV remaining on a quartz substrate, after UV-irradiation on a spin-coated thin film of all-cis PpPV, followed by rinsing twice with CHCl₃, is clearly dependent on the molecular weight and terminal groups of the starting polymer. It has been found that (Z)-4-(2-bromoethyl)phenyl group facilitates the photo-induced insolubilization to a notable extent. The insolubilized films exhibit the hole mobility ($\mu_{\text{FET}}$) of up to $1.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. 
Introduction

Recently, a great deal of effort has been devoted to the development of polymeric semiconductors, which are key components of flexible electronic devices such as organic field effective transistors (OFETs) and organic light-emitting diodes (OLEDs). Poly(p-phenylenevinylene)s (PPVs) are among the most studied ones. A distinct advantage of polymeric materials is the accessibility of thin films by solution processes such as spin-coating and dip-coating, which enable easy and low-cost fabrication of devices. Since it is difficult to gain high device performance with a single component, most of the devices are composed of multilayer structures. In this connection, several methods of insolubilizing thin films have been developed to avoid interfusion of polymer layers upon multi-coating; the establishment of well-defined interfacial boundary of thin films is an essential requirement for achieving high device performance. The most extensively investigated method is the use of photo- or thermal-cross-linkable polymers. Alternatively, soluble precursors coated onto substrates are thermally converted to insoluble polymers. Although insoluble films of PPVs are generally prepared by the latter method, it has been known that the resulting polymers often involve structural defects due to incomplete reactions.

The author’s group has recently found that PPVs gain a very unique film-forming property when the vinylene linkages are highly regulated to cis geometry. Thus, all-cis PPVs \((M_n = 4700 \text{ and } 5000)\), prepared by Suzuki–Miyaura-type polycondensation of \((Z,Z)-1,4-\) and \((Z,Z)-1,3\)-bis(2-bromoethenyl)benzenes with 2,5-dioctyloxy-benzene-1,4-diboronic acid, form highly amorphous films by spin-coating. Interestingly, the resulting films become insoluble in common organic solvents under UV light, along with cis-to-trans isomerization of vinylene linkages. Although one may assume that photoisomerization giving all-trans PPV with a rigid framework causes the insolubilization phenomenon, it has been found that PPV \((M_n = 7200, M_w/M_n = 1.81)\) independently prepared in all-trans form remains soluble under UV light, showing the presence of additional factors other than all-cis...
configuration. Consequently, it has been considered that some primary structures unique to all-cis PPVs cause the photo-induced insolubilization.

In this Chapter, all-cis poly(p-phenylenevinylene)s (PpPVs) were prepared with a range of molecular weights and end-group structures, and examined their performance by a quantitative method. It has been found that the presence of a 2-bromoethenyl group at the polymer end is of significance for insolubilization to proceed efficiently under UV light. The insolubilized films exhibit the carrier mobility ($\mu_{\text{FET}}$) of up to $1.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. 
Results and Discussion

Preparation of All-cis PpPVs. As previously reported, the palladium-catalyzed polycondensation of (Z,Z)-1,4-bis(2-bromoethenyl)benzene (1) with 2,5-dioctyloxybenzene-1,4-diboronic acid (2) forms two types of all-cis PpPVs (3 and 4) having different terminal structures (Scheme 1).\textsuperscript{16a} Polymer 3 bears (Z)-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus, whereas 4 is substituted with 2,5-dioctyloxyphenyl groups at both ends. Detailed examination of all-cis PpPV with $M_n$ of 2400 has revealed that the catalytic polycondensation reaction produces “type I polymer” mainly composed of 3. This product can be converted to “type II polymer” predominantly consisting of 4 by end-capping with 2,5-dioctylxybenzeneboronic acid (5).\textsuperscript{16b}

**Scheme 1. Synthetic Routes to All-cis PpPVs**
Table 1 lists the all-cis PpPVs prepared in this study. The molecular weights of type I polymers (Ia–h) vary with catalytic conditions, especially with the absence or presence of Bu₄NBr as a phase transfer catalyst. The polymers with $M_n$ of less than 3000 are obtained in the absence of Bu₄NBr, while the molecular weight increases up to 8100 in the presence of Bu₄NBr (1 equiv). The bromine content in low molecular weight polymers (Ib and Ie) is in a 20% relative error range of the calculated values, showing the predominance of 3 in these polymers. On the other hand, the bromine content in higher molecular weight polymers (Id, If, and Ig) is apparently lower than the calculated values; the content of 3 is estimated to be 56–76% of the whole polymers.

### Table 1. Specifications and Performance on Insolubilization of All-cis PpPVs

<table>
<thead>
<tr>
<th>all-cis PpPV</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Br (%)</th>
<th>insolubilized PpPV (%)</th>
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<tbody>
<tr>
<td>Ia</td>
<td>1800</td>
<td>1.39</td>
<td>$e$</td>
<td>36</td>
</tr>
<tr>
<td>Ib</td>
<td>2800</td>
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<td>2.29 [2.85]</td>
<td>33</td>
</tr>
<tr>
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<td>2.63 [2.28]</td>
<td>59</td>
</tr>
<tr>
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<td>2.79</td>
<td>1.10 [1.70]</td>
<td>56</td>
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<td>4800</td>
<td>2.20</td>
<td>$e$</td>
<td>64</td>
</tr>
<tr>
<td>If</td>
<td>6600</td>
<td>3.14</td>
<td>0.68 [1.21]</td>
<td>85</td>
</tr>
<tr>
<td>Ig</td>
<td>7000</td>
<td>2.69</td>
<td>0.87 [1.14]</td>
<td>84</td>
</tr>
<tr>
<td>Ih</td>
<td>8100</td>
<td>3.93</td>
<td>$e$</td>
<td>89</td>
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<td>2400</td>
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<td>0.41 [3.33]</td>
<td>2</td>
</tr>
<tr>
<td>IIb</td>
<td>5000</td>
<td>1.03</td>
<td>$e$</td>
<td>11</td>
</tr>
<tr>
<td>IIc</td>
<td>7700</td>
<td>1.11</td>
<td>$e$</td>
<td>35</td>
</tr>
</tbody>
</table>

*a* Determined by GPC calibration based on polystyrene standards. *b* Determined by elemental analysis. The numbers in brackets are calculated values for pure 3 having the corresponding $M_n$ values. *c* See text. *d* Separated from IIa by recycle GPC. *e* Not determined.
Type II polymer IIa was prepared by palladium-catalyzed polycondensation, followed by end-capping of 3 with 5.\textsuperscript{16b} Since the end-capping did not proceed cleanly with higher molecular weight polymers, IIb and IIc were separated from IIa by recycle GPC.

**Photo-induced Insolubilization of All-cis PpPVs.** Figure 1 illustrates the experimental procedure for photo-induced insolubilization. (i) A thin film of type I or type II polymer was prepared from a CHCl\textsubscript{3} solution (2.0 wt\%) by spin-coating, and (ii) irradiated with UV light (\(\lambda = 300–400\ \text{nm}, \ 21.0\ \text{mW cm}^{-2}\)) for 1 h at room temperature under vacuum. (iii) The irradiated film was rinsed twice with CHCl\textsubscript{3} and dried.

Figure 2 compares the UV-vis absorption spectra of the films at steps (i)–(iii). (i) The thin film of all-cis PpPV exhibits the \(\pi-\pi^*\) transition at 388 nm. (ii) This absorption disappears upon UV-irradiation, and a strong absorption assignable to the \(\pi-\pi^*\) transition of all-trans PPV appears at 466 nm instead. (iii) The absorption remains after rinsing with CHCl\textsubscript{3}, though the intensity drops to a certain extent. In the case of Ig as a type I polymer, 84\% of the intensity of spectrum (ii) was preserved in spectrum (iii). This value corresponds

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**Figure 1.** Experimental procedure for photo-induced insolubilization of all-cis PpPVs.
Photo-induced Insolubilization of PpPVs

Figure 2. UV–vis absorption spectra of all-cis PpPV (Ig) in thin film, before and after UV-irradiation (i and ii), and after rinsing with CHCl₃ (iii).

to the percentage of PpPV insolubilized by UV-irradiation. The data for Ia–h and IIa–e are listed in Table 1.

Figure 3 plots the insolubilized PpPV percentages as the function of number-average molecular weights of the starting all-cis PpPVs. There are two lines of correlations, corresponding to type I and type II polymers, respectively. It is seen that type I polymers have much higher performance on insolubilization than type II polymers, showing a promotion effect of the (Z)-4-(2-bromoethenyl)phenyl group. It is also clear that the higher molecular weight polymer tends to remain in the higher percentage.

There is a possibility that the insolubilization is caused by cross-linking of polymer chains via photochemical reactions such as [2+2] cycloaddition of vinylene units and radical addition of C–Br bonds to vinylene linkages, where shortening of the effective π-conjugation length should occur to a considerable extent. However, no notable blue shifts of the λ_max values were observed for spectra (ii) and (iii) in Figure 2, as compared with that of all-trans PpPV (Mₙ = 7200, M_w/M_n = 1.81) independently prepared.¹⁷
Therefore, the author considered an alternative mechanism of photo-induced insolubilization caused by supra-molecular interactions. It has been already confirmed that all-cis PpPV cast from a solution remains amorphous for a few hours. The amorphous all-cis PpPV has a low glass transition temperature \((T_g; \text{ca. } 0 \, ^\circ\text{C})\) and is in the liquid state at room temperature. Therefore, the all-cis PpPV molecules are expected to be highly mobile in thin films. In this situation, all-trans PpPV molecules generated by photo-isomerization will easily form a highly aligned structure with the aid of \(\pi-\pi\) stacking between the conjugated skeletons. It has been also known that halogen atoms on aromatic molecules facilitate the formation of \(\pi\)-stacks. Thus the higher performance of type I polymer on insolubilization will be attributed to Br···Br interaction between PpPV molecules.

**OFET Properties of Insolubilized PpPVs.** The thin films of all-trans PpPVs formed by photo-induced insolubilization of all-cis PpPVs exhibited carrier mobility in OFET devices.
Photovoltaic Insolubilization of PpPVs

 fabricated on Si–SiO$_2$ substrates (see Experimental Section).$^{19,20}$ Table 2 summarizes the results. Although all-cis PpPVs simply coated on substrates were insulators, they exhibited hole mobility after UV-irradiation at room temperature for 1 h. The mobility was improved with increasing molecular weights of the starting polymers, and further by rinsing the film with toluene (entry 4). It was also confirmed in a separate experiment that all-trans PpPV ($M_n = 7200, M_w/M_n = 1.81$) prepared by Hiyama-type polycondensation is an insulator even after photo-irradiation. These observations may also indicate the occurrence of molecular alignment during the photo-induced insolubilization of all-cis PPVs in thin films.

<table>
<thead>
<tr>
<th>entry</th>
<th>all-cis PpPV</th>
<th>carrier mobility ($\mu_{FET}, \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n^a$</td>
<td>$M_w/M_n^a$</td>
</tr>
<tr>
<td>1</td>
<td>5900</td>
<td>3.61</td>
</tr>
<tr>
<td>2</td>
<td>7700</td>
<td>2.69</td>
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<td>3</td>
<td>11200</td>
<td>2.66</td>
</tr>
<tr>
<td>4</td>
<td>34600$^b$</td>
<td>1.47</td>
</tr>
</tbody>
</table>

$^a$Determined by GPC calibration based on polystyrene standards. $^b$Separated from an all-cis PpPV ($M_n = 15700$) by recycle GPC. $^c$Not determined.

Conclusions

In conclusion, it has been confirmed that the performance on photo-induced insolubilization notably depends on molecular weights and terminal structures of the starting all-cis PPVs. Type I polymers with $M_n > 6600$ are insolubilized in 84–89% probability. The resulting films of all-trans PpPVs exhibited the carrier mobility of up to $1.6 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in OFET devices.
Experimental Section

**General Considerations.** All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P$_2$O$_5$ (Merck, SICAPENT). 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, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL/min at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; $M_n = 980–1,920,000$). Recycling preparative GPC was carried out on a JAI LC918U equipped with two preparative GPC columns (JAIGEL-1H-A and -2H-A). CHCl$_3$ was used as the mobile phase with a flow rate of 3.8 mL/min. $^1$H NMR spectra were recorded in CDCl$_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300.10 MHz. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin coating of PpPVs 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 was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). The following compounds were synthesized according to literatures: Pd(PPh$_3$)$_4$, $^{21}$ (Z,Z)-1,4-(2-bromoethenyl)benzene (1), $^{22}$ 2,5-dioctyloxybenzene-1,4-diboronic acid (2), $^{23}$ 2,5-dioctyloxybenzenboronic acid (5), $^{24}$ and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene.$^{16b}$ All-cis PpPVs (Ia–h and IIa)$^{16a,b}$ and all-trans PpPV$^{17}$ were prepared according to literatures. All other chemicals were obtained from commercial suppliers and used without further purification.

**Photo-induced Insolubilization of PpPV.** A solution of PpPV 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 PpPV 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 N₂ atmosphere, and then 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 (λ_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 CHCl₃ (each 3 mL) with light shaking, dried under vacuum at room temperature, and examined by UV-vis absorption spectroscopy.

**Preparation of all-cis PpPVs with High Molecular Weights (entries 3 and 4 in Table 2).** 

(Z,Z)-1 (173 mg, 0.600 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (352 mg, 0.600 mmol) and methyltrioctylammonium chloride (Aliquat® 336; 24.3 mg, 0.0600 mmol) were dissolved in toluene (3 mL), and 2.0 M aqueous Na₂CO₃ (0.90 mL, 1.8 mmol) and [Pd(PPh₃)₄] (10.4 mg, 9.00 µmol) were added. The mixture was vigorously stirred under reflux for 24 h in the dark. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (8 mL), washed with water, and then poured into a vigorously stirred MeOH/CH₂Cl₂ (5/1, 180 mL). A yellow precipitate of all-cis PpPV was collected by membrane filter (0.5 µm), washed with MeOH, and dried under vacuum at room temperature overnight (254 mg, 92% yield, Mₕ = 11200, M_w/Mₙ = 2.66). The polymer with Mₙ = 34600 (M_w/Mₙ = 1.47) was separated from this product by recycle GPC.

**Measurement of Carrier Mobility.** All manipulations were carried out in an argon-filled glove box. An OFET device was fabricated in a top-contact configuration on a p-type Si wafer as a gate electrode (one-side polished, < 0.02 Ω resistance, Furuuchi Chemical Co.) with 3000-Å-thick SiO₂ (Cᵢ = 11 nF cm⁻²) as a dielectric film. A plate was cut and washed in 2-propanol under ultrasonic wave and under boiling. A thin film of PpPVs as the active layer (ca. 30 nm thick) was deposited on the Si/SiO₂ substrate by spin-coating a 0.1–0.5 wt% solution in CHCl₃ at 100–8000 rpm for 60 s, and dried under vacuum at room temperature, and irradiated by a Xe lamp (λ_max = 365 nm, 23.0 mW cm⁻²) for 1 h. On the top
of the thin film, gold films (30 nm) as source and drain electrodes were deposited through a mask. A drain-source channel length \( (L) \) and width \( (W) \) were 20 \( \mu m \) and 5 mm, respectively. Characteristics of OFET devices were evaluated at room temperature with two source meters (2400, Keithley Instruments Inc.). Carrier mobility \( (\mu_{\text{FET}}) \) was calculated in the saturation regime \( (V_d = 100 \text{ V}) \) of the \( I_d \) using the following equation,

\[
I_d = \frac{W C_i}{2L} \mu_{\text{FET}} (V_g - V_t)^2
\]

where \( C_i \) is the capacitance of the SiO\(_2\) insulator, and \( V_g \) and \( V_t \) are the gate and threshold voltages, respectively. In another case, the PPV thin film was rinsed twice with toluene (1 mL) after UV-irradiation, and examined in a similar manner.

References and Notes


(19) All-cis PpPVs with higher molecular weights (entries 3 and 4 in Table 2) were obtained by modified catalytic conditions reported in Experimental Section.


Chapter 2

Stereocntrolled Synthesis and Photochemical Properties of All-cis and All-trans Poly(m-phenylenevinylene)s

Abstract

All-cis and all-trans isomers of poly[(arylenevinylene)-alt-(5-octyloxy-1,3-phenylenevinylene)]s having three kinds of arylene groups (PmPVs: arylene = m-phenylene (1a), p-phenylene (1b), 4,4'-biphenylene (1c)) have been synthesized in almost perfect stereoregularities by two types palladium-catalyzed polycondensation reactions. Suzuki–Miyaura-type polycondensation of (Z,Z)-bis(2-bromoethenyl)arenes with 5-octyloxy-1,3-benzenediboronic acid pinacolate affords all-cis 1a–c, whereas Hiyama-type polycondensation of (E,E)-bis(2-silylethenyl)arenes with 5-octyloxy-1,3-diiodobenzene forms all-trans 1a–c. The resulting polymers having relatively short effective π-conjugation lengths, interrupted by m-phenylene units, undergo two-way photoisomerization, giving PmPVs containing cis- and trans-vinylene groups in nearly 1:1 ratios, irrespective of the configurations of the staring polymers.
Chapter 2

Introduction

The author’s group recently succeeded for the first time in synthesizing all-cis poly(p-phenylenevinylene)s (PpPVs), in which vinylene linkages in the polymer chain are entirely stereoregulated to cis geometry.\(^1\) The all-cis PpPVs are readily isomerized to the corresponding all-trans PpPVs in solution under UV-irradiation.\(^1a\) The cis-to-trans isomerization also takes place when thin films of all-cis PpPVs are exposed to UV light. Interestingly, as described in Chapter 1, the PpPV films are insolubilized during the photoisomerization. Furthermore, the insolubilized films exhibit the carrier mobility (\(\mu_{\text{FET}}\)) of up to \(1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). A key to this unique phenomenon is the “one-way photoisomerization” of PpPVs. The one-way photoisomerization of conjugated alkenes has been documented in several instances.\(^2,3\) Thus, while stilbene undergoes two-way photoisomerization to give a cis-rich mixture in the photostationary state, the alkenes with extended \(\pi\)-conjugation systems are isomerized solely from the cis to trans isomer.

Chart 1

\[
\begin{align*}
\text{Ar} &= \begin{array}{c}
\text{Ar} \\
\text{(a)} \\
\text{(b)} \\
\text{(c)}
\end{array} \\
\text{all-cis PmPV (1a–c)} \\
\text{all-trans PmPV (1a–c)}
\end{align*}
\]
This chapter deals with the synthesis and photoisomerization of all-cis and all-trans poly(m-phenylenevinylene)s (PmPVs). Although photoisomerization of alkene has been extensively studied for small molecules, the related studies on polymeric alkenes have been scarce. In this study, the author has compared photoisomerization behaviors between PmPVs (1a–e) and their constitution units (2–5) (Chart 1). Unlike PpPVs with extended \( \pi \)-conjugation systems, PmPVs have relatively short effective \( \pi \)-conjugation lengths, interrupted by \( m \)-phenylene units. It has been found that PmPVs undergo two-way photoisomerization both in solution and in thin films.
Results and Discussion

Synthesis and Characterization of PmPVs. All-cis and all-trans PmPVs were synthesized by Suzuki–Miyaura-type\textsuperscript{1,5} and Hiyama-type polycondensation,\textsuperscript{6,7} respectively (eqs 1 and 2). The reactions of (Z,Z)-bis(2-bromoethenyl)arenes (6a–c) with 5-octyloxy-1,3-benzenediboronic acid ester (7) in toluene at 80 °C in the presence of [Pd(PPh\textsubscript{3})\textsubscript{4}] (1.0 mol%), aqueous KOH (3 M, 3 equiv), and Bu\textsubscript{4}NBr (1 equiv) for 24 h formed all-cis isomers of 1a–c in 84–97% yields (entries 1–3 in Table 1). On the other hand, the reactions of (E,E)-bis(2-silylethenyl)arenes (8a–c) with 5-octyloxy-1,3-diiodobenzene (9) in THF at room temperature in the presence of [Pd(μ-Cl)(η\textsuperscript{3}-allyl)]\textsubscript{2} (5 mol%) and Bu\textsubscript{4}NF (2 equiv) for 100 h afforded all-trans isomers of 1a–c in quantitative yields (entries 4–6 in Table 1).

The polymers were isolated as gummy pastes (all-cis PmPVs) or powdery solids (all-trans PmPVs), respectively. The geometry and stereoregularity of vinylene linkages were unequivocally confirmed by NMR spectroscopy. Table 2 compares the NMR data of 1a–c with those of 2–5. The vinylic carbons of cis and trans isomers showed clearly different chemical shifts at around δ 130 and 129, respectively. Moreover, the OCH\textsubscript{2} proton signals of octyloxy groups were well separated from each other. As seen from the \textsuperscript{1}H NMR spectra in
All-cis and All-trans Poly(m-phenylenevinylene)s

Table 1. Synthesis of All-cis and All-trans PmPVs (1a–c)

<table>
<thead>
<tr>
<th>entry</th>
<th>product</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$M_n$&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$M_w / M_n$&lt;sup&gt;b&lt;/sup&gt;</th>
<th>cis/trans&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>all-cis 1a</td>
<td>97</td>
<td>3800</td>
<td>3.43</td>
<td>&gt;99/1</td>
</tr>
<tr>
<td>2</td>
<td>all-cis 1b</td>
<td>84</td>
<td>4300</td>
<td>4.23</td>
<td>&gt;99/1</td>
</tr>
<tr>
<td>3</td>
<td>all-cis 1c</td>
<td>95</td>
<td>4700</td>
<td>5.27</td>
<td>&gt;99/1</td>
</tr>
<tr>
<td>4</td>
<td>all-trans 1a</td>
<td>&gt;99</td>
<td>5200</td>
<td>1.75</td>
<td>&lt;1/99</td>
</tr>
<tr>
<td>5</td>
<td>all-trans 1b</td>
<td>&gt;99</td>
<td>4200</td>
<td>1.47</td>
<td>&lt;1/99</td>
</tr>
<tr>
<td>6</td>
<td>all-trans 1c</td>
<td>&gt;99</td>
<td>8300</td>
<td>2.35</td>
<td>&lt;1/99</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield of MeOH-insoluble polymer.  <sup>b</sup>Determined by GPC calibration based on polystyrene standards.  <sup>c</sup>Determined by <sup>1</sup>H NMR.

Figure 1, the signals of cis- and trans-1a appeared at $\delta$ 3.59 and 4.03, respectively. The cis/trans ratios listed in Table 1 were evaluated from the peak intensities of these signals.

![Figure 1](image)

Figure 1. <sup>1</sup>H NMR spectra of (A) cis-1a and (B) trans-1a in CDCl$_3$ at room temperature.
### Table 2. Selected NMR Data of PmPVs (1a–c) and Model Compounds (2–5)\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^{13})C NMR (\delta_{C=C})</th>
<th>(^{1}H) NMR (\delta_{OCH_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>all-cis 1a</td>
<td>130.1, 130.1</td>
<td>3.59</td>
</tr>
<tr>
<td>all-cis 1b</td>
<td>130.0, 130.0</td>
<td>3.62</td>
</tr>
<tr>
<td>all-cis 1c</td>
<td>130.4, 130.2</td>
<td>3.63</td>
</tr>
<tr>
<td>(Z)-2</td>
<td>130.3, 130.3</td>
<td>3.77</td>
</tr>
<tr>
<td>(Z,Z)-3</td>
<td>130.4, 130.0</td>
<td>3.59</td>
</tr>
<tr>
<td>(Z,Z)-4</td>
<td>130.2, 130.0</td>
<td>3.81</td>
</tr>
<tr>
<td>(Z,Z)-5</td>
<td>130.4, 129.8</td>
<td>3.80</td>
</tr>
<tr>
<td>all-trans 1a</td>
<td>129.0, 128.8</td>
<td>4.03</td>
</tr>
<tr>
<td>all-trans 1b</td>
<td>128.7, 128.5</td>
<td>4.05</td>
</tr>
<tr>
<td>all-trans 1c</td>
<td>128.6, 128.6</td>
<td>4.07</td>
</tr>
<tr>
<td>(E)-2</td>
<td>128.9, 128.7</td>
<td>4.00</td>
</tr>
<tr>
<td>(E,E)-3</td>
<td>129.2, 128.5</td>
<td>4.05</td>
</tr>
<tr>
<td>(E,E)-4</td>
<td>128.6, 128.5</td>
<td>4.00</td>
</tr>
<tr>
<td>(E,E)-5</td>
<td>128.8, 128.4</td>
<td>4.01</td>
</tr>
</tbody>
</table>

*Measured in CDCl\(_3\) at room temperature.

**Photoisomerization of PmPVs. (a) In Solution.** The all-cis and all-trans PmPVs were dissolved in benzene (4.0 mg L\(^{-1}\)) and irradiated with a Xe lamp (\(\lambda_{\text{max}} = 365\) nm, 0.87 mW cm\(^{-2}\)) in a quartz cell under a nitrogen atmosphere at room temperature. The sample solutions were monitored at intervals by UV-vis spectroscopy. Figure 2 shows the change of absorption spectra of all-cis 1c (A) and all-trans 1c (B). Upon UV-irradiation, the absorption of all-cis isomer (\(\lambda_{\text{max}} = 328\) nm) increased whereas that of all-trans isomer (\(\lambda_{\text{max}} = 366\) nm) decreased to achieve the photostationary state.\(^{10}\) The cis content in the equilibrium mixture was estimated as 53% according to the following equation: cis (%) = \((A_{\text{trans}} - A_{\text{pss}})/(A_{\text{trans}} - A_{\text{cis}}) \times 100\), where \(A_{\text{trans}}\) and \(A_{\text{cis}}\) stand for the absorbance of all-trans and all-cis isomers at
Table 3 summarizes the results of photoisomerization of 1a–c. All polymers undergo two-way photoisomerization to give PmPVs containing cis- and trans-vinylene groups. It is seen that the cis/trans ratios in the photostationary state ([cis/trans]_{pss}) are quite different from those of 2–5. Meeting the general expectations, the trans contents in 2–5 in the photostationary state increase with elongation of the effective \( \pi \)-conjugation lengths in the order 2 < 3 < 4 < 5. In contrast, the cis/trans ratios of 1a–c converge at nearly 1:1 irrespective of the arylene groups. Since the \( \lambda_{\text{max}} \) values of 1a–c are in good agreement with those of 3–5, respectively, it is convincing that each polymer has almost the same \( \pi \)-conjugation length as the corresponding constitution. Nevertheless, the vinylene groups reach the equilibrium in a nearly 1:1 ratio.

It is known that the two-way photoisomerization of stilbene proceeds mainly via a singlet excited state with the 90°-twisted form as the potential minimum. The deactivation takes place solely from this perpendicular conformation to give a mixture of cis and trans isomers. However, when the alkene unit is integrated into an extended \( \pi \)-conjugated system,
the alkene molecule possibly undergoes intersystem crossing to give a triplet excited state, where the 90°-twisted form is no longer the potential minimum, and therefore the alkene molecule changes its conformation from the cis form to the trans form, passing through the perpendicular triplet state. As a result, the one-way photoisomerization becomes predominant to give a trans-rich or all-trans product. The variation in the cis/trans ratios observed for 2–5 is fully consistent with this trend. On the other hand, as for the polymeric alkenes 1a–c, there is a possibility that the 90°-twisted form still remains as the energy minimum on the excited potential surface to avoid the steric congestion within the molecule. In this case, the excited state should be deactivated from the twisted form to give PmPVs containing both cis- and trans-vinylene groups.

Table 3. Photoisomerization of 1a–c and 2–5 in Benzene

<table>
<thead>
<tr>
<th>compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>time (sec)</th>
<th>cis/trans&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>all-cis</td>
<td>all-trans</td>
<td>pss&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1a</td>
<td>273&lt;sup&gt;e&lt;/sup&gt;</td>
<td>311</td>
<td>307</td>
</tr>
<tr>
<td>1b</td>
<td>319</td>
<td>372</td>
<td>368</td>
</tr>
<tr>
<td>1c</td>
<td>328</td>
<td>366</td>
<td>350</td>
</tr>
<tr>
<td>2</td>
<td>280&lt;sup&gt;e&lt;/sup&gt;</td>
<td>310</td>
<td>—&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>269&lt;sup&gt;e&lt;/sup&gt;</td>
<td>313</td>
<td>—&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>318</td>
<td>362</td>
<td>362</td>
</tr>
<tr>
<td>5</td>
<td>328</td>
<td>356</td>
<td>356</td>
</tr>
</tbody>
</table>

<sup>a</sup> A benzene solution of the compound (4.0 mg L<sup>-1</sup>) was irradiated with a Xe lamp (λ<sub>max</sub> = 365 nm, 0.87 mW cm<sup>-2</sup>) in a quartz cell under a nitrogen atmosphere at room temperature. Photoisomerization was followed by UV-vis spectroscopy. <sup>b</sup> pss = photostationary state. <sup>c</sup> The time to achieve the photostationary state starting from cis isomer. <sup>d</sup> See text. <sup>e</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup> Unable to be observed due to overlap with the absorbance of benzene.
(b) In Thin Films. All-cis and all-trans PmPVs underwent two-way photoisomerization in thin films as well. Figure 3 shows the change of UV-vis absorption spectra of 1a in thin films, which were prepared from a CHCl₃ solution (2.0 wt%) by spin-coating on a quartz substrate, and irradiated with a Xe lamp (λ_max = 365 nm, 21.0 mW cm⁻²) under vacuum at room temperature. It was noted that the absorption maxima of all-cis and all-trans 1a are red-shifted by 2 and 11 nm, respectively, as compared with those in solution. Although the photoisomerization could not be evaluated quantitatively because of the change of the thickness of films depending on the experimental runs, the spectroscopic change in this figure indicates a very similar cis/trans ratio to the solution system. Interestingly, the photo-irradiated films remained on the substrate in high percentages (>90%) after rising twice with CHCl₃. Thus, PmPVs were found to undergo photo-induced insolubilization in thin films.

**Figure 3.** Changes of UV–vis absorption spectra of all-cis 1a (A) and all-trans 1a (B) under UV-irradiation in thin films.
Conclusions

Suzuki–Miyaura-type and Hiyama-type polycondensation reactions provide all-cis and all-trans PmPVs in perfect stereoregularity, respectively. The resulting polymers undergo two-way photoisomerization of vinylene units in solution as well as in thin films, giving PmPVs containing cis- and trans-vinylene groups in nearly 1:1 ratios. This behavior is quite different from that of the corresponding poly(p-phenylenevinylene)s (PpPVs), which undergo one-way photoisomerization to all-trans isomers in the photostationary state. Thus, it has been evidenced that the photoisomerization behaviors of poly(phenylenevinylene)s are dependent on the effective $\pi$-conjugation lengths of polymer chains.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P$_2$O$_5$ (Merck, SICAPENT). 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 $\delta$ (ppm), referenced to the $^1$H (residual protons) and $^{13}$C signals of deuterated solvents. Mass spectra were measured with a Shimadzu QP-500 GC-mass spectrometer (EI, 70 eV) or Shimadzu GC-MS QP2010 (EI, 70 eV). Melting points were measured with a Yanaco MP-S3 instrument. 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, 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; $M_n = 980–1920000$). Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PmPV was performed with a Mikasa spin coater 1H-DX2. Photo-irradiation 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 was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). THF (Wako, dehydrated) was used as received. The following compounds were synthesized according to literatures: \([\text{Pd}(\text{PPh}_3)_4]_1^{11} \), \([\text{Pd}(\mu-\text{Cl})(\eta^3-\text{allyl})]_2^{12} \), \([\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]^{13} \), \((Z,Z)-\text{bis}(2\text{-bromoethenyl})\text{arenes (6a–e)}^{14} \), \((E,E)-1,4\text{-bis}[2-\{(3,5\text{-bis-(trifluoromethyl)phenyl})\text{dimethylsilyl}\}\text{ethenyl} ]\text{benzene (8b)}^{7} \), \(\text{dimethyl[3,5-bis(trifluoromethyl)phenyl]silane}^{15} \) \(4,4'-\text{diethynylbiphenyl (12)}^{16} \), \((Z)-\text{styryl bromide (17)}^{17} \) and \((E)-2-\{(3,5\text{-bis(trifluoromethyl)phenyl})\text{dimethylsilyl}\}\text{ethenyl} ]\text{benzene (20)}^{18} \) All other chemicals were obtained from commercial suppliers and used without further purification.

**Synthesis of Monomers. (a)** \(1,3\text{-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-octyloxybenzene (7)}^{10} \)

\[
\begin{align*}
\begin{array}{c}
\text{F} \quad \text{Br} \\
\text{Br} \quad \text{OC}_8\text{H}_{17} \quad \text{BuOK} \quad \text{NMP} \\
\end{array}
\end{align*}
\]

This compound was prepared by a two-step procedure. (i) To a solution of 1,3-dibromo-5-fluorobenzene (10; 9.02 g, 35.5 mmol) and \(N\)-methylpyrrolidione (4.93 g, 49.8 mmol) in 1-octanol (35.5 mL) was added potassium \(\text{tert-butoxide (14.0 g, 124 mmol) at 0 °C.}
\) The mixture was stirred at 0 °C for 15 min, then stirred at room temperature for 4 h. Water (50 mL) was added, and the resulting mixture was extracted with \(\text{Et}_2\text{O (4 × 75 mL).} \) The combined extracts were washed with water (100 mL) and brine (100 mL), dried over \(\text{MgSO}_4\), and concentrated under reduced pressure. Remaining 1-octanol was removed by bulb-to-bulb distillation (35 Pa, 55 °C). The residue was purified by flash column chromatography (SiO\(_2\), hexane) to afford 1,3-dibromo-5-octyloxybenzene (11) as a colorless oil (11.9 g, 92% yield).

\(^1\text{H NMR (CDCl}_3\): } \delta \ 7.22 \ (t, J = 1.6 \text{ Hz, 1H, H}}_2 \text{ of Ar}), 6.98 \ (d, J = 1.7 \text{ Hz, 2H, H}}^5 \text{ of Ar}), 3.91 \ (t, J = 6.5 \text{ Hz, 2H, OCH}_2), 1.76 \ (m, 2H, CH}_2), 1.45–1.29 \ (\text{several m, 10H, CH}_2), 0.91–0.87 \ (m, 3H, CH}_3). \ ^{13}\text{C}^{1}\text{H}^1\text{NMR (CDCl}_3\): } \delta \ 160.3 \ (s, C}_5 \text{ of Ar}), 126.1 \ (s, C}_1^{13} \text{ of Ar}), 123.0 \ (s, C}_2 \text{ of Ar}), 116.9 \ (s, C}_6^{4} \text{ of Ar}), 68.6 \ (s, \text{OCH}_2), 31.8, 29.2, 29.2, 29.0, 25.9, 22.6
(each s, CH$_2$), 14.1 (s, CH$_3$). MS, $m/z$ (relative intensity, %): 364 (M$^+$, 6), 254 (14), 252 (30), 250 (16), 83 (15), 71 (22), 70 (21), 69 (14), 57 (50), 56 (20), 55 (37), 43 (90), 42 (17), 41 (100). Anal. Calcd. for C$_{14}$H$_{20}$Br$_2$O: C, 40.90; H, 4.90. Found: C, 40.78; H, 4.78.

(ii) A mixture of 11 (3.96 g, 10.9 mmol), bis(pinacolato)diboron (6.07 g, 23.9 mmol), [PdCl$_2$(dppf)] (477 mg, 0.652 mmol), potassium acetate (6.40 g, 65.2 mmol), and DMF (109 mL) was stirred at 80 °C for 5 h. The solvent was removed by bulb-to-bulb distillation (5 kPa, 70 °C). The residue was dissolved in CH$_2$Cl$_2$, filtered through a Celite pad, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (SiO$_2$) eluted with CH$_2$Cl$_2$/hexane (9/1, 1% Et$_3$N), and subsequently recrystallized from CH$_2$Cl$_2$/pentane at –30 °C to afford 7 as a white solid (2.42 g, 48% yield).

Mp: 55 °C. $^1$H NMR (CDCl$_3$): δ 7.85 (s, 1H, H$_2$ of Ar), 7.42 (s, 2H, H$_{4,6}$ of Ar), 3.99 (t, $J$ = 6.4 Hz, 2H, OCH$_2$), 1.80–1.71 (m, 2H, CH$_2$), 1.50–1.25 (several m, 10H, CH$_2$), 1.33 (s, 24H, C(CH$_3$)$_2$), 0.91–0.87 (m, 3H, CH$_3$). $^{13}$C($^1$H)NMR (CDCl$_3$): δ 158.2 (s, C$_5$ of Ar), 133.4 (s, C$_2$ of Ar), 123.4 (s, C$_{4,6}$ of Ar), 83.7 (s, C(CH$_3$)$_2$), 67.8 (s, OCH$_2$), 31.8, 29.4, 29.3, 29.3, 26.1 (each s, CH$_2$), 24.8 (s, C(CH$_3$)$_2$), 22.7 (s, CH$_2$), 14.1 (s, CH$_3$). MS, $m/z$ (relative intensity, %): 459 (M$^+$ + 1, 5), 458 (M$^+$, 17), 457 (M$^+$ – 1, 8), 260 (14), 101 (10), 83 (41), 69 (16), 59 (14), 57 (40), 55 (42), 43 (100), 42 (24), 41 (72). Anal. Calcd. for C$_{26}$H$_{44}$B$_2$O$_5$: C, 68.15; H, 9.68. Found: C, 67.90; H, 9.88.

(b) ($E$,$E$)-Bis[2-{(3,5-bis(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]arenes (8).$^7$

A typical procedure is reported for 8a. To a solution of dimethyl-[3,5-bis(trifluoromethyl)phenyl]silane (3.01 g, 11.0 mmol) and 1,3-diethynylbenzene (12a; 253 mg, 2.01 mmol) in CH$_2$Cl$_2$ (8 mL) was added [RuHCl(CO)(PPh$_3$)$_3$] (191 mg, 0.201 mmol). The mixture was stirred for 5 h, and concentrated under reduced pressure. The
residue was subjected to flash column chromatography (SiO$_2$) eluted with hexane/CH$_2$Cl$_2$ (40/1). The crude product was purified by recycle GPC to afford 8a as a colorless oil (745 mg, 53% yield, $(E,E) > 99\%$). Compound 8c was similarly prepared and isolated as a pale yellow solid by recrystallization from CH$_2$Cl$_2$/hexane (85% yield).

8a. $^1$H NMR (CDCl$_3$): $\delta$ 7.97 (br s, 4H, H$_2^2,6^2$ of C$_6$H$_3$), 7.87 (br s, 2H, H$_2^4$ of C$_6$H$_3$), 7.57 (s, 1H, H$_1^2$ of C$_6$H$_4$), 7.42–7.39 (m, 2H, H$_{4,6}^4$ of C$_6$H$_4$), 7.34 (dd, $J = 8.6, 6.4$ Hz, 1H, H$_5^5$ of C$_6$H$_4$), 7.00 (d, $J = 19.2$ Hz, 2H, C$_6$H$_4$CH=), 6.57 (d, $J = 19.1$ Hz, 2H, =CHSi), 0.52 (s, 12H, Si(CH$_3$)$_2$).

$^{13}$C{$_1^1$H}NMR (CDCl$_3$): $\delta$ 146.5 (s, C$_6$H$_4$CH=), 142.3 (s, C$_1^1$ of C$_6$H$_3$), 138.0 (s, C$_1^1,3^3$ of C$_6$H$_4$), 133.6 (s, C$_2^2,6^2$ of C$_6$H$_3$), 130.9 (q, $^2J_{FC} = 33$ Hz, C$_3^3,5^5$ of C$_6$H$_3$), 129.0 (s, C$_5^5$ of C$_6$H$_4$), 126.9 (C$_4^4,6^6$ of C$_6$H$_4$), 125.2 (s, =CHSi), 124.9 (s, C$_2^2$ of C$_6$H$_4$), 123.6 (q, $^1J_{FC} = 273$ Hz, CF$_3$), 122.9 (septet, $^3J_{FC} = 4$ Hz, C$_4^4$ of C$_6$H$_3$), –2.8 (s, Si(CH$_3$)$_2$).

Anal. Calcd. for C$_{30}$H$_{26}$F$_{12}$Si$_2$: C, 53.72; H, 3.91. Found: C, 53.52; H, 3.86.

8c. Mp: 144 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.97 (br s, 4H, H$_2^2,6^2$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), 7.87 (br s, 2H, H$_2^4$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), 7.61 (d, $J = 8.3$ Hz, 4H, H$_{2,6}^2,6^2$ of C$_{12}$H$_8$), 7.54 (d, $J = 8.4$ Hz, 4H, H$_{3,5}^3,5^5$ of C$_{12}$H$_8$), 7.02 (d, $J = 19.1$ Hz, 2H, C$_6$H$_4$CH=), 6.57 (d, $J = 19.1$ Hz, 2H, =CHSi), 0.52 (s, 12H, Si(CH$_3$)$_2$).

$^{13}$C{$_1^1$H}NMR (CDCl$_3$): $\delta$ 146.3 (s, C$_6$H$_4$CH=), 142.4 (s, C$_1^1$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), 140.7 (s, C$_1^{1,1'}$ of C$_{12}$H$_8$), 136.8 (s, C$_{4,4'}^4$ of C$_{12}$H$_8$), 133.6 (s, C$_2^2$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), 130.8 (q, $^2J_{FC} = 33$ Hz, C$_3^3,5^5$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), 127.2 (each s, C$_{2,6}^2,2^2,6^6$ and C$_{3,5,3'}^3,5^5,3''$ of C$_{12}$H$_8$), 124.8 (s, =CHSi), 123.9 (q, $^1J_{FC} = 273$ Hz, CF$_3$), 122.9 (septet, $^3J_{FC} = 4$ Hz, C$_4^4$ of C$_6$H$_3^{-3,5}$-(CF$_3$)$_2$), –2.8 (s, Si(CH$_3$)$_2$).

Anal. Calcd. for C$_{36}$H$_{30}$F$_{12}$Si$_2$: C, 57.90; H, 4.05. Found: C, 57.75; H, 4.25.

(c) 1,3-Diiodo-5-octyloxybenzene (9).
This compound was prepared by a two-step procedure. (i) To a solution of 11 (7.91 g, 21.7 mmol) in THF (109 mL) was added dropwise a 1.59 M solution of n-BuLi in hexane (14.2 mL, 22.4 mmol) at –78 °C. After the mixture was stirred at this temperature for 1 h, trimethylsilyl chloride (3.1 mL, 24 mmol) was slowly added. The solution was stirred at –78 °C for 1 h and then at room temperature for 1 h. This process was repeated with a 1.59 M solution of n-BuLi in hexane (16.5 mL, 26.0 mmol) and trimethylsilyl chloride (3.1 mL, 24 mmol). Water (200 mL) was added, and the mixture was extracted with diethyl ether (4 × 100 mL). The combined extracts were washed with brine (100 mL), dried over MgSO₄, evaporated under reduced pressure, and then purified by flash column chromatography (SiO₂, hexane) to give 1,3-bis(trimethylsilyl)-5-octyloxybenzene (13) as a colorless oil (7.32 g, 96% yield). ¹H NMR (CDCl₃): δ 7.22 (t, J = 0.9 Hz, 1H, H⁴ of Ar), 7.03 (d, J = 0.8 Hz, 2H, H²,⁶ of Ar), 3.98 (t, J = 6.6 Hz, 2H, OCH₂), 1.83–1.74 (m, 2H, CH₂), 1.52–1.24 (several m, 10H, CH₂), 0.92–0.86 (m, 3H, CH₃), 0.27 (s, 18H, Si(CH₃)₃). ¹³C{¹H}NMR (CDCl₃): δ 157.9 (s, C¹ of Ar), 141.3 (s, C⁴ of Ar), 130.2 (s, C₃,₅ of Ar), 119.6 (s, C²,⁶ of Ar), 67.7 (s, OCH₂), 31.8, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH₂), 14.1 (s, CH₃), –1.1 (s, Si(CH₃)₃). MS, m/z (relative intensity, %): 352 (M⁺ + 2, 4), 351 (M⁺ + 1, 10), 350 (M⁺, 29), 336 (11), 335 (35), 238 (13), 225 (6), 224 (16), 223 (70), 179 (10), 75 (9), 74 (9), 73 (100), 69 (28), 57 (21), 55 (35), 45 (26), 43 (86), 41 (78). Anal. Calcd. for C₂₀H₃₈O₂Si₂: C, 68.50; H, 10.92. Found: C, 68.73; H, 10.74.

(ii) To a solution of 13 (6.42 g, 18.3 mmol) in CH₂Cl₂ (92 mL) was added dropwise a 1.0 M solution of iodine chloride in CH₂Cl₂ (55 mL, 55 mmol) at –78 °C. The reaction solution was stirred at this temperature for 2 h. An aqueous Na₂S₂O₅ solution (10%, 100 mL) was added, and the mixture was extracted with CH₂Cl₂ (4 × 100 mL). The combined extracts were washed with brine (100 mL), dried over MgSO₄, and evaporated under reduced pressure, to give a pale yellow solid, which was purified by flash column chromatography (SiO₂, hexane), and subsequently recrystallized from CHCl₃/EtOH at –30 °C to afford 9 as a white solid (6.69 g, 80% yield). Mp: 37 °C. ¹H NMR (CDCl₃): δ 7.60 (t, J = 1.2 Hz, 1H, H² of Ar), 7.20 (d, J = 1.2 Hz, 2H, H⁴,⁶ of Ar), 3.88 (t, J = 6.5 Hz, 2H, OCH₂), 1.79–1.70 (m, 2H, CH₂),
All-cis and All-trans Poly(m-phenylenevinylene)s

1.46–1.24 (several m, 10H, CH₂), 0.92–0.86 (m, 3H, CH₃). \(^{13}\)C{\(^{1}\)H} NMR (CDCl₃): \(\delta\) 159.9 (s, C⁵ of Ar), 137.2 (s, C² of Ar), 123.4 (s, C⁴,⁶ of Ar), 94.6 (s, C¹,² of Ar), 68.5 (s, OCH₂), 31.8, 29.3, 29.2, 29.0, 25.9, 22.6 (each s, CH₂), 14.1 (s, CH₃). MS, m/z (relative intensity, %): 459 (M⁺ + 1, 2), 458 (M⁺, 13), 347 (3), 346 (45), 75 (13), 69 (12), 63 (19), 57 (33), 55 (31), 43 (82), 42 (11), 41 (100). Anal. Calcd. for C₁₄H₂₀I₂O: C, 36.70; H, 4.40. Found: C, 36.59; H, 4.46.

Synthesis of All-cis PmPVs (1). A typical procedure is reported for all-cis 1a. To a solution of 6a (28.8 mg, 0.100 mmol), 7 (45.8 mg, 0.100 mmol), and Bu₄NBr (32.2 mg, 0.100 mmol) in toluene (0.5 mL) were added [Pd(PPh₃)₄] (1.2 mg, 1.0 µmol) and 3.0 M aqueous KOH (0.10 mL, 0.30 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The mixture was extracted with CH₂Cl₂ (1 mL), washed with water (3 × 3 mL), and then poured into a vigorously stirred MeOH (50 mL). A pale yellow, sticky precipitate of all-cis 1a was collected by decantation, washed with MeOH, and dried under vacuum at room temperature overnight (32.3 mg, 97% yield).

All-cis 1a. Pale yellow gummy paste. \(^{1}\)H NMR (CDCl₃): \(\delta\) 7.20–6.90 (m, C₆H₄), 6.73–6.67 (m, H² of C₆H₃OR), 6.64–6.57 (m, H⁴,⁶ of C₆H₃OR), 6.44–6.32 (m, CH=CH), 3.84–3.70 (m, OCH₂ of terminal C₆H₄OR), 3.59 (t, J = 6.5 Hz, OCH₂), 1.80–1.49 and 1.43–1.14 (m, CH₂), 0.92–0.80 (m, CH₃). \(^{13}\)C{\(^{1}\)H} NMR (CDCl₃): \(\delta\) 158.7 (s, C⁵ of C₆H₃OR), 138.3 (s, C¹,³ of C₆H₃OR), 137.1 (s, C¹,³ of C₆H₄), 130.1, 130.1 (each s, CH=CH), 129.7 (s, C⁵ of C₆H₄), 127.8 (s, C² of C₆H₄), 127.6 (s, C⁴,⁶ of C₆H₄), 122.2 (s, C² of C₆H₃OR), 113.8 (s, C⁴,⁶ of C₆H₃OR), 67.8 (s, OCH₂), 31.9, 29.3, 29.3, 29.1, 26.1, 22.7 (each s, CH₂), 14.1 (s, CH₃).

All-cis 1b. Yellow gummy paste. \(^{1}\)H NMR (CDCl₃): \(\delta\) 7.06 (br, C₆H₄), 6.74 (br, H² of C₆H₃OR), 6.62 (br, H⁴,⁶ of C₆H₃OR), 6.43 (br, CH=CH), 3.62 (t, J = 6.3 Hz, OCH₂), 1.73–1.53 and 1.43–1.16 (m, CH₂), 0.92–0.80 (m, CH₃). \(^{13}\)C{\(^{1}\)H} NMR (CDCl₃): \(\delta\) 158.8 (s, C⁵ of C₆H₃OR), 138.5 (s, C¹,³ of C₆H₃OR), 135.9 (s, C¹,⁴ of C₆H₄), 130.0, 130.0 (each s, CH=CH), 128.9 (s, C²,³,⁵,⁶ of C₆H₄), 121.8 (s, C² of C₆H₃OR), 113.7 (s, C⁴,⁶ of C₆H₃OR), 83.8
(s, C(CH$_3$)$_2$ of terminal BOC(CH$_3$)$_2$), 67.8 (s, OCH$_2$), 31.8, 29.3, 29.3, 29.1, 25.9 (each s, CH$_2$), 24.8 (s, C(CH$_3$)$_2$ of terminal BOC(CH$_3$)$_2$), 22.7, 14.1 (s, CH$_3$).

**All-cis 1c.** Yellow solid. $^1$H NMR (CDCl$_3$): δ 7.52–7.15 (m, H$_{2,6,2',6'}$ and H$_{3,5,3',5'}$ of C$_{12}$H$_8$), 6.83 (br, H$_6$ of C$_6$H$_3$OR), 6.68 (br, H$_{2,4}$ of C$_6$H$_3$OR), 6.53–6.42 (m, CH=CH), 3.63 (br, 2H, OCH$_2$), 1.74–1.47 (br, 2H, CH$_2$), 1.45–1.07 (br, 10H, CH$_2$), 1.31 (s, C(CH$_3$)$_2$ of terminal BOC(CH$_3$)$_2$), 0.92–0.74 (br, 3H, CH$_3$).

$^{13}$C{$^1$H} NMR (CDCl$_3$): δ 158.9 (s, C$_3$ of C$_6$H$_3$), 139.1, 138.6, 136.1 (each s, C$_{1,1'}$ and C$_{4,4'}$ of C$_{12}$H$_8$ and C$_{1,5}$ of C$_6$H$_3$), 130.4, 130.2 (each s, CH=CH), 129.4, 126.4 (each s, C$_{2,6,2',6'}$ and C$_{3,5,3',5'}$ of C$_8$H$_{12}$), 121.7 (s, C$_6$ of C$_6$H$_3$), 113.8 (s, C$_{2,4}$ of C$_6$H$_3$), 83.8 (s, C(CH$_3$)$_2$ of terminal BOC(CH$_3$)$_2$), 67.8 (s, OCH$_2$), 31.8, 29.3, 29.2, 29.1, 25.9, 22.7 (each s, CH$_2$), 24.8 (s, C(CH$_3$)$_2$ of terminal BOC(CH$_3$)$_2$), 14.1 (s, CH$_3$).

**Synthesis of All-trans PmPVs (1).** A typical procedure is reported for of all-trans 1a.

To a solution of 8a (67.7 mg, 0.100 mmol) and 9 (45.4 mg, 0.100 mmol) in THF (1.0 mL) were added [Pd($\mu$-Cl)(η$^3$-allyl)]$_2$ (1.8 mg, 5.0 µmol) and a 1.0 M solution of Bu$_4$NF·3H$_2$O in THF (0.20 mL, 0.20 mmol). The mixture was stirred at room temperature for 100 h. The resulting suspension was poured into a vigorously stirred MeOH (50 mL). A white precipitate of all-trans 1a was collected by a membrane filter (0.5 µm), washed with MeOH, and dried under vacuum at room temperature overnight (36.0 mg, >99% yield).

**All-trans 1a.** White solid. $^1$H NMR (CDCl$_3$): δ 8.03 (br s, H$_{2,6}$ of C$_6$H$_3$-3,5-(CF$_3$)$_2$ of terminal CH=CHSi(CH$_3$)$_2$Ar), 7.87 (br s, H$_1$ of C$_6$H$_3$-3,5-(CF$_3$)$_2$ of terminal CH=CHSi(CH$_3$)$_2$Ar), 7.71–7.57 (m, H$_3$ of C$_6$H$_4$), 7.50–7.25 (m, H$_{4,6}$ and H$_5$ of C$_6$H$_4$), 7.25–7.04 (m, H$_2$ of C$_6$H$_3$OR and CH=CH), 7.04–6.86 (m, H$_{2,6}$ of C$_6$H$_3$OR), 4.11–3.88 (m, OCH$_2$), 1.90–1.73 and 1.57–1.20 (m, CH$_2$), 0.93–0.83 (m, CH$_3$), 0.52 (s, CH$_3$ of terminal CH=CHSi(CH$_3$)$_2$Ar). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 159.8 (s, C$_5$ of C$_6$H$_3$OR), 138.8 (s, C$_{1,3}$ of C$_6$H$_3$OR), 137.6 (s, C$_{1,3}$ of C$_6$H$_4$), 129.0, 128.8 (each s, CH=CH), 128.8 (s, C$_2$ of C$_6$H$_4$), 125.9 (s, C$_{4,6}$ of C$_6$H$_4$), 124.8 (s, C$_5$ of C$_6$H$_4$), 118.0 (s, C$_2$ of C$_6$H$_3$OR), 111.8 (s, C$_{4,6}$ of C$_6$H$_3$OR), 68.1 (s, OCH$_2$), 31.9, 29.4, 29.3, 26.1, 22.7 (each s, CH$_2$), 14.1 (s, CH$_3$), –2.8 (s, CH$_3$ of terminal CH=CHSi(CH$_3$)$_2$Ar).
**All-trans 1b.** Yellow solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.97 (br s, \(H^{2,6}\) of C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar), 7.87 (br s, \(H^1\) of C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar), 7.54 (s, C\(_6\)H\(_4\)), 7.20–7.03 (m, \(H^2\) of C\(_6\)H\(_3\) and CH=CH), 6.99 (s, \(H^{2,6}\) of C\(_6\)H\(_3\)), 4.05 (t, \(J = 6.4\) Hz, OCH\(_2\)), 3.95 (t, \(J = 6.4\) Hz, OCH\(_2\) of terminal C\(_6\)H\(_3\)IOC\(_8\)H\(_{17}\)), 1.90–1.73 (m, CH\(_2\)), 1.57–1.22 (m, CH\(_2\)), 0.93–0.83 (m, CH\(_3\)), 0.52 (s, CH\(_3\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar). \(^{13}\)C\({\{}^1\)H\} NMR (CDCl\(_3\)): \(\delta\) 159.8 (s, C\(_5\) of C\(_6\)H\(_3\)), 138.9 (s, C\(^{1,3}\) of C\(_6\)H\(_3\)), 136.7 (C\(^{1,4}\) of C\(_6\)H\(_4\)), 128.7, 128.5 (each s, CH=CH), 127.0 (s, C\(^{2,3,5,6}\) of C\(_6\)H\(_4\)), 118.0 (s, \(C^2\) of C\(_6\)H\(_3\)), 111.7 (s, C\(^{4,6}\) of C\(_6\)H\(_3\)), 94.7 (s, \(C^1\) of C\(_6\)H\(_3\) of terminal C\(_6\)H\(_3\)IOC\(_8\)H\(_{17}\)), 68.1 (s, OCH\(_2\)), 31.8, 29.4, 29.3, 29.3, 26.1, 22.7 (each s, CH\(_2\)), 14.1 (s, CH\(_3\)), –2.7 (s, CH\(_3\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar).

**All-trans 1c.** Yellowish green solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.98 (br s, \(H^{2,6}\) of C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar), 7.88 (br s, \(H^4\) of C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar), 7.70–7.50 (m, 8H, \(H^{2,6,2',6'}\) and \(H^{3,5,3',5'}\) of C\(_{12}\)H\(_8\)), 7.23–7.00 (m, 5H, \(H^{2,4}\) and \(H^6\) of C\(_6\)H\(_3\) and 2 \(\times\) CH=CH), 6.57 (d, \(J = 18.8\) Hz, CH=CH of terminal CH=CHSi(CH\(_3\))\(_2\)Ar), 4.07 (t, \(J = 6.4\) Hz, OCH\(_2\)), 3.97 (t, \(J = 6.4\) Hz, OCH\(_2\) of terminal C\(_6\)H\(_3\)IOC\(_8\)H\(_{17}\)), 1.89–1.75 (br, 2H, CH\(_2\)), 1.56–1.25 (br, 10H, CH\(_2\)), 0.94–0.87 (br, 3H, CH\(_3\)), 0.53 (s, CH\(_3\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar). \(^{13}\)C\({\{}^1\)H\} NMR (CDCl\(_3\)): \(\delta\) 159.9, 159.8 (each s, \(C^5\) of C\(_6\)H\(_3\) and \(C^2\) of C\(_6\)H\(_3\) of terminal C\(_6\)H\(_3\)IOC\(_8\)H\(_{17}\)), 139.7, 138.9, 136.3 (each s, \(C^{1,1'}\) and \(C^{4,4'}\) of C\(_{12}\)H\(_8\) and \(C^{1,5}\) of C\(_6\)H\(_3\)), 128.6 (br s, CH=CH), 127.0 (br s, \(C^{2,6,2',6'}\) and \(C^{3,5,3',5'}\) of C\(_8\)H\(_{12}\)), 118.1 (s, \(C^2\) of C\(_6\)H\(_3\)), 111.7 (s, \(C^{4,6}\) of C\(_6\)H\(_3\)), 94.7 (s, \(C^1\) of C\(_6\)H\(_3\) of terminal C\(_6\)H\(_3\)IOC\(_8\)H\(_{17}\)), 68.1 (s, OCH\(_2\)), 31.9, 29.4, 29.3, 26.2, 22.7 (each s, CH\(_2\)), 14.2 (s, CH\(_3\)), –2.7 (s, CH\(_3\) of terminal CH=CHSi(CH\(_3\))\(_2\)Ar).
Synthesis of Model Compounds. (a) \((Z)-1\text{-octyloxy-3-styrylbenzene ((Z)-2).}\)

This compound was prepared by a three-step procedure. (i) To a solution of \(m\)-bromophenol (14; 5.50 g, 31.8 mmol) and 1-bromooctane (9.21 g, 47.7 mmol) in DMF (32 mL) was added \(\text{K}_2\text{CO}_3\) (11.0 g, 79.5 mmol). The mixture was stirred at 60 °C for 3 h. After cooling to room temperature, water (100 mL) was added, and the mixture was extracted with \(\text{Et}_2\text{O}\) (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over \(\text{MgSO}_4\), evaporated under reduced pressure, and then purified by flash column chromatography (\(\text{SiO}_2,\) hexane), giving 1-bromo-3-octyloxybenzene (15) as a colorless oil (8.08 g, 89% yield). \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta\) 7.11 (t, \(J = 8.2\) Hz, 1H, \(H^5\) of Ar), 7.07–7.02 (m, 2H, \(H_2^2,6\) of Ar), 6.81 (ddd, \(J = 8.1, 2.3, 1.0\) Hz, 1H, \(H^4\) of Ar), 3.92 (t, \(J = 6.5\) Hz, 2H, OCH\(_2\)), 1.81–1.72 (m, 2H, CH\(_2\)), 1.48–1.22 (several m, 10H, CH\(_2\)), 0.92–0.86 (m, 2H, CH\(_3\)). \(^{13}\text{C}\{^1\text{H}\}\) NMR (CDCl\(_3\)): \(\delta\) 159.9 (s, \(C^3\) of Ar), 130.4 (s, \(C^5\) of Ar), 123.5 (s, \(C^6\) of Ar), 122.8 (s, \(C^1\) of Ar), 117.7 (s, \(C^2\) of Ar), 113.5 (s, \(C^4\) of Ar), 68.2 (s, OCH\(_2\)), 31.8, 29.3, 29.2, 29.1, 26.0, 22.7 (each s, CH\(_2\)), 14.1 (s, CH\(_3\)). MS, \(m/z\) (relative intensity, %): 286 (\(M^+ + 1, 5\)), 284 (\(M^+ – 1, 5\)), 174 (50), 172 (52), 76 (6), 71 (15), 70 (11), 69 (11), 57 (36), 56 (13), 55 (32), 43 (84), 42 (17), 41 (100). Anal. Calcd. for C\(_{14}\)H\(_{21}\)BrO: C, 58.95; H, 7.42. Found: C, 58.55; H, 7.42.

(ii) To a solution of 15 (3.99 g, 14.0 mmol) in THF (70 mL) was added dropwise a 1.59 M solution of \(\text{n-BuLi}\) in hexane (9.2 mL, 15 mmol) at –78 °C. After the mixture was stirred
at this temperature for 1.5 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.20 g, 28.0 mmol) was slowly added. The solution was stirred at –78 °C for 1 h and then at room temperature for 7 h. Water (100 mL) was added, and the mixture was extracted with diethyl ether (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over MgSO$_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ (5/1, 1% Et$_3$N)), giving 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-octyloxybenzene (16) as a colorless oil (3.58 g, 77% yield).

$^1$H NMR (CDCl$_3$): δ 7.38 (d, $J = 7.1$ Hz, 1H, H$_6$ of Ar), 7.32 (d, $J = 2.5$ Hz, 1H, H$_5$ of Ar), 7.28 (t, $J = 8.2$ Hz, 1H, H$_2$ of Ar), 7.00 (ddd, $J = 8.2$, 2.7, 0.9 Hz, 1H, H$_4$ of Ar), 3.98 (t, $J = 6.5$ Hz, 2H, OCH$_2$), 1.81–1.72 (m, 2H, CH$_2$), 1.51–1.23 (several m, 10H, CH$_2$), 1.34 (s, 12H, C(CH$_3$)$_2$), 0.91–0.87 (m, 2H, CH$_3$).

$^{13}$C{$_1$H}NMR (CDCl$_3$): δ 158.6 (s, C$_3$ of Ar), 128.9 (s, C$_5$ of Ar), 126.9 (s, C$_6$ of Ar), 119.6 (s, C$_2$ of Ar), 118.2 (s, C$_4$ of Ar), 83.8 (s, C(CH$_3$)$_2$), 67.9 (s, OCH$_2$), 31.8, 29.4, 29.3, 26.1 (each s, CH$_2$), 24.9 (s, C(CH$_3$)$_2$), 14.1 (s, CH$_3$). The $^{13}$C signal of C$_1$ of Ar was obscure due to coupling with quadrupolar $^{11}$B nucleus. MS, m/z (relative intensity, %): 333 (M$^+$ + 1, 3), 332 (M$^+$, 13), 220 (24), 219 (8), 205 (19), 135 (13), 134 (86), 133 (5), 121 (16), 120 (19), 83 (12), 69 (15), 59 (11), 57 (32), 55 (36), 43 (100), 42 (24), 41 (99). Anal. Calcd. for C$_{20}$H$_{33}$BO$_3$: C, 72.29; H, 10.01. Found: C, 72.25; H, 9.95.

(iii) To a solution of (Z)-styryl bromide (17; (Z) > 99%, 39.5 mg, 0.216 mmol), 16 (68.2 mg, 0.205 mmol), and Bu$_4$NBr (69.6 mg, 0.216 mmol) in toluene (1.1 mL) were added [Pd(PPh$_3$)$_4$] (2.5 mg, 2.2 µmol) and 3.0 M aqueous KOH (0.22 mL, 0.65 mmol). The mixture was stirred at 80 °C for 3 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ (10/1)), giving (Z)-2 ((E)/(Z) < 1/99) as a colorless oil (62.5 mg, 99% yield). $^1$H NMR (CDCl$_3$): δ 7.28–7.09 (m, 6H, Ph and H$_5$ of C$_6$H$_4$OR), 6.81 (d, $J = 7.6$ Hz, 1H, H$_6$ of C$_6$H$_4$OR), 6.77 (s, 1H, H$_2$ of C$_6$H$_4$OR), 6.73 (dd, $J = 8.1$, 2.4 Hz, 1H, H$_4$ of C$_6$H$_4$OR), 6.60, 6.56 (each d, $J = 12.3$ Hz, 2H, CH=CH), 3.77 (t, $J = 6.6$ Hz, 2H, OCH$_2$), 1.72–1.63 (m, 2H, CH$_2$), 1.43–1.23 (several m, 10H, CH$_2$), 0.92–0.87 (m, 3H, CH$_3$). $^{13}$C{$_1$H}NMR (CDCl$_3$): δ 158.9 (s, C$_1$ of C$_6$H$_4$OR), 138.5 (s,
C\textsuperscript{3} of C\textsubscript{6}H\textsubscript{4}OR, 137.3 (s, C\textsuperscript{1} of Ph), 130.3, 130.3 (each s, CH=CH), 129.2 (s, C\textsuperscript{5} of C\textsubscript{6}H\textsubscript{4}OR), 128.9, 128.2 (each s, C\textsuperscript{2,6} and C\textsuperscript{3,5} of Ph), 127.1 (s, C\textsuperscript{4} of Ph), 121.3 (s, C\textsuperscript{6} of C\textsubscript{6}H\textsubscript{4}OR), 114.3, 114.0 (each s, CH\textsubscript{2}), 127.1 (s, C\textsuperscript{4} of Ph), 121.3 (s, C\textsuperscript{6} of C\textsubscript{6}H\textsubscript{4}OR), 114.3, 114.0 (each s, CH\textsubscript{2}), 14.1 (s, CH\textsubscript{3}). MS, \textit{m/z} (relative intensity, %): 309 (M\textsuperscript{+} + 1, 9), 308 (M\textsuperscript{+}, 36), 197 (11), 196 (73), 195 (42), 181 (14), 178 (24), 177 (14), 167 (19), 166 (10), 165 (22), 152 (15), 57 (22), 43 (85), 42 (10), 41 (100). Anal. Calcd. for C\textsubscript{20}H\textsubscript{28}O: C, 85.66; H, 9.15. Found: C, 85.79; H, 9.30.

(b) \((E)-1\text{-octyloxy-3-styrylbenzene} ((E)-2).\)

\[
\begin{align*}
\text{18} & \xrightarrow{\text{K}_2\text{CO}_3, \text{DMF}} \text{19} \\
& \xrightarrow{[\text{Pd(OAc)}\text{2}, \text{Bu}_4\text{NF}, \text{THF}]} (E)-2
\end{align*}
\]

(SiR\textsubscript{3} = SiMe\textsubscript{2}(C\textsubscript{6}H\textsubscript{3}(CF\textsubscript{3})\textsubscript{2}-3,5))

This compound was prepared by a two-step procedure. (i) To a solution of \textit{m}-iodophenol (18; 3.02 g, 13.7 mmol) and 1-iodooctane (3.97 g, 20.6 mmol) in DMF (14 mL) was added K\textsubscript{2}CO\textsubscript{3} (4.74 g, 34.3 mmol). The mixture was stirred at 60 °C for 4 h. After cooling to room temperature, water (100 mL) was added, and the mixture was extracted with Et\textsubscript{2}O (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over MgSO\textsubscript{4}, evaporated under reduced pressure, and then purified by flash column chromatography (SiO\textsubscript{2}, hexane), giving 1-iodo-3-octyloxybenzene (19) as a colorless oil (4.47 g, 98% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 7.27–7.22 (m, 2H, H\textsubscript{2,6} of Ar), 6.97 (t, \(J = 8.2\) Hz, 1H, H\textsuperscript{5} of Ar), 6.87–6.82 (m, 1H, H\textsuperscript{4} of Ar), 3.91 (t, \(J = 6.5\) Hz, 2H, OCH\textsubscript{2}), 1.81–1.72 (m, 2H, CH\textsubscript{2}), 1.48–1.22 (m, 10H, CH\textsubscript{2}), 0.92–0.86 (m, 2H, CH\textsubscript{3}). \textsuperscript{13}C\textsubscript{1}(\textsuperscript{1}H) NMR (CDCl\textsubscript{3}): \(\delta\) 159.7 (s, C\textsuperscript{3} of Ar), 150.7 (s, C\textsuperscript{5} of Ar), 129.6 (s, C\textsuperscript{6} of Ar), 123.6 (s, C\textsuperscript{2} of Ar), 114.2 (s, C\textsuperscript{4} of Ar), 94.4 (s, C\textsuperscript{1} of Ar), 68.2 (s, OCH\textsubscript{2}), 31.8, 29.3, 29.2, 29.1, 26.0, 22.7 (each s, CH\textsubscript{2}), 14.1 (s, CH\textsubscript{3}). MS, \textit{m/z} (relative intensity, %): 332 (M\textsuperscript{+}, 11), 220 (71), 93 (11), 76 (13), 71 (12), 69
All-cis and All-trans Poly(m-phenylenevinylene)s

(i) To a solution of \( (E)-2\)-{(3,5-bis(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]-benzene (20; \( (E) > 99\% \), 36.5 mg, 0.0975 mmol) and 19 (34.1 mg, 0.103 mmol) in THF (1 mL) were added \([Pd(OAc)_2]\) (2.3 mg, 10 \( \mu \)mol) and 1.0 M solution of Bu_4NF·3H_2O in THF (0.10 mL, 0.10 mmol). The mixture was stirred at room temperature for 1 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (10/1)), giving \( (E)-2 \) \( ((E)/(Z) > 99/1) \) as a white solid (27.1 mg, 90% yield). Mp: 33 °C. ^1H NMR (CDCl_3): \( \delta \) 7.51 (d, \( J = 7.5 \) Hz, 2H, H_2,6 of Ph), 7.36 (t, \( J = 7.5 \) Hz, 2H, H_1,3 of Ph), 7.29–7.23 (m, 2H, H_4 of Ph and H_5 of C_6H_4OR), 7.11, 7.07 (each d, \( J = 16.4 \) Hz, 2H, CH=CH), 7.11–7.07 (m, 1H, H_4 of C_6H_4OR), 7.05 (s, 1H, H_2 of C_6H_4OR), 6.81 (dd, \( J = 8.2, 2.4 \) Hz, 1H, H_6 of C_6H_4OR), 4.00 (t, \( J = 6.5 \) Hz, 2H, OCH_2), 1.85–1.75 (m, 2H, CH_2), 1.52–1.20 (several m, 10H, CH_2), 0.93–0.84 (m, 3H, CH_3). ^13C{^1H}NMR (CDCl_3): \( \delta \) 159.5 (s, C_1 of C_6H_4OR), 138.7 (s, C_3 of C_6H_4OR), 137.3 (s, C_1 of Ph), 129.6 (s, C_5 of C_6H_4OR), 128.9 (s, CH=CH), 128.7 (s, CH=CH), 127.6 (s, C_4 of Ph), 128.7, 126.5 (each s, C_2,6 and C_3,5 of Ph), 119.1 (s, C_6 of C_6H_4OR), 113.8, 112.3 (each s, C_2 and C_4 of C_6H_4OR), 68.0 (s, OCH_2), 31.8, 29.4, 29.3, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, \( m/z \) (relative intensity, %): 309 (M^+ + 1, 7), 308 (M^+, 28), 197 (9), 196 (60), 195 (33), 181 (11), 179 (16), 178 (19), 177 (11), 167 (17), 166 (8), 165 (18), 152 (12), 57 (20), 55 (25), 43 (84), 42 (11), 41 (100). Anal. Calcd. for C_{20}H_{28}O: C, 85.66; H, 9.15. Found: C, 85.30; H, 9.24.

(c) \( (Z,Z)-1,3\)-distyryl-5-octyloxybenzene \((Z,Z)-3\).

\[ \text{[Pd(PPh_3)_4]} \text{aq KOH Bu}_4\text{NBr} \rightarrow (Z,Z)-3 \]
To a solution of 17 (88.9 mg, 0.486 mmol), 7 (101 mg, 0.221 mmol), and Bu$_4$NBr (71.2 mg, 0.221 mmol) in toluene (1.1 mL) were added [Pd(PPh$_3$)$_4$] (12.8 mg, 11.0 µmol) and 3.0 M aqueous KOH (0.22 mL, 0.66 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ (10/1)) and then recycle GPC, giving (Z,Z)-3 ((Z,Z) > 99%) as a yellow oil (64.8 mg, 71% yield). 

$^1$H NMR (CDCl$_3$): $^\text{δ}$ 7.26–7.17 (m, 10H, Ph), 6.73 (s, 1H, H$_4$ of C$_6$H$_3$), 6.62 (s, 2H, H$_{2,6}$ of C$_6$H$_3$), 6.54 (d, $J$ = 12.2 Hz, 2H, CH=CH), 6.45 (d, $J$ = 12.2 Hz, 2H, CH=CH), 3.59 (t, $J$ = 6.6 Hz, 2H, OCH$_2$), 1.62–1.54 (m, 2H, CH$_2$), 1.42–1.18 (several m, 10H, CH$_2$), 0.93–0.86 (m, 3H, CH$_3$).

$^{13}$C{$_^1$H}NMR (CDCl$_3$): $^\text{δ}$ 158.7 (s, C$_1$ of C$_6$H$_3$), 138.4 (C$_{3,5}$ of C$_6$H$_3$), 137.2 (s, C$_1$ of Ph), 130.4, 130.0 (each s, CH=CH), 128.9 (C$_{3,5}$ of Ph), 128.1 (s, C$_{2,6}$ of Ph), 127.1 (s, C$_4$ of Ph), 122.0 (s, C$_4$ of C$_6$H$_3$), 113.8 (s, C$_{2,6}$ of C$_6$H$_3$), 67.7 (s, OCH$_2$), 31.8, 29.2, 29.2, 29.0, 25.9, 22.7 (each s, CH$_2$), 14.1 (s, CH$_3$). MS, m/z (relative intensity, %): 412 (M$^+$ + 2, 6), 411 (M$^+$ + 1, 31), 410 (M$^+$, 100), 299 (13), 298 (52), 297 (10), 279 (12), 219 (16), 207 (28), 203 (11), 179 (12), 165 (15), 141 (12), 115 (10), 91 (38), 69 (10), 57 (16), 55 (15). Anal. Calcd. for C$_{30}$H$_{34}$O: C, 87.76; H, 8.35. Found: C, 87.57; H, 8.37.

(d) (E,E)-1,3-distyryl-5-octyloxybenzene ((E,E)-3).

\[
\begin{align*}
\text{[Pd(µ-Cl)(η^5-allyl)]}_2 + \text{Bu}_4\text{NF} & \rightarrow (E,E)-3 \\
\text{Bu}_4\text{NF} & \text{THF}
\end{align*}
\]

(SiR$_3$ = SiMe$_2$(C$_6$H$_5$(CF$_3$)$_2$-3,5))

To a solution of (E)-20 (137 mg, 0.366 mmol) and 9 (76.2 mg, 0.166 mmol) in THF (1.7 mL) were added [Pd(µ-Cl)(η^3-allyl)]$_2$ (3.0 mg, 8.3 µmol) and a 1.0 M solution of Bu$_4$NF·3H$_2$O in THF (0.37 mL, 0.37 mmol). The mixture was stirred at room temperature for 24 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ (10/3)) and then recycle GPC, giving (E,E)-3 ((E,E) >
99%) as a white solid (33.8 mg, 50% yield). Mp: 53–54 °C. \( ^1\)H NMR (CDCl\(_3\)): \( \delta \) 7.53 (d, \( J = 7.5 \) Hz, 4H, H\(^2,6\) of Ph), 7.37 (t, \( J = 7.5 \) Hz, 4H, H\(^3,5\) of Ph), 7.27 (t, \( J = 7.3 \) Hz, 2H, H\(^4\) of Ph), 7.25 (s, 1H, H\(^4\) of C\(_6\)H\(_3\)), 7.15 (d, \( J = 16.3 \) Hz, 2H, CH=CH), 7.09 (d, \( J = 16.3 \) Hz, 2H, CH=CH), 6.98 (s, 2H, H\(^2,6\) of C\(_6\)H\(_3\)), 4.05 (t, \( J = 6.6 \) Hz, 2H, OCH\(_2\)), 1.87–1.79 (m, 2H, CH\(_2\)), 1.54–1.24 (several m, 10H, CH\(_2\)), 0.93–0.87 (m, 3H, CH\(_3\)). 

\( ^{13}\)C\{\( ^1\)H\}NMR (CDCl\(_3\)): \( \delta \) 159.8 (s, C\(^1\) of C\(_6\)H\(_3\)), 138.9 (C\(^3,5\) of C\(_6\)H\(_3\)), 137.2 (s, C\(^1\) of Ph), 129.2, 128.5 (each s, CH=CH), 127.7 (s, C\(^4\) of Ph), 128.7 (s, C\(^3,5\) of Ph), 126.6 (s, C\(^2,6\) of Ph), 117.9 (s, C\(^4\) of C\(_6\)H\(_3\)), 111.7 (s, C\(^2,6\) of C\(_6\)H\(_3\)), 68.1 (s, OCH\(_2\)), 31.8, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH\(_2\)), 14.1 (s, CH\(_3\)). Anal. Calcd. for C\(_{30}\)H\(_{34}\)O: C, 87.76; H, 8.35. Found: C, 87.51; H, 8.39.

(e) (Z,Z)-Bis(3-octyloxystyryl)arenes ((Z,Z)-4 and 5).

\[
(Z,Z)-6b,c + 2 \rightarrow (Z,Z)-4,5
\]

A typical procedure is reported for (Z,Z)-4. To a solution of (Z,Z)-6b ((E)/(Z) < 1/99) (109 mg, 0.300 mmol), 16 (219 mg, 0.660 mmol), and Bu\(_4\)NBr (96.7 mg, 0.300 mmol) in toluene (1.5 mL) were added [Pd(PPh\(_3\))\(_4\)] (17.3 mg, 15.0 µmol) and 3.0 M aqueous KOH (0.30 mL, 0.90 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO\(_2\), hexane/CH\(_2\)Cl\(_2\) (8/1)) and then recycle GPC, giving the title compound ((Z,Z) > 99%) as a pale yellow oil (124 mg, 91% yield). (Z,Z)-5 was similarly synthesized using (Z,Z)-6c ((Z,Z) > 99%) in 84% yield.

(Z,Z)-4. Pale yellow oil. \( ^1\)H NMR (CDCl\(_3\)): \( \delta \) 7.13 (s, 4H, p-phenylene), 7.11 (t, \( J = 7.9 \) Hz, 2H, H\(^5\) of C\(_6\)H\(_4\)OR), 6.82 (d, \( J = 7.7 \) Hz, 2H, H\(^6\) of C\(_6\)H\(_4\)OR), 6.79 (s, 2H, H\(^2\) of C\(_6\)H\(_4\)OR), 6.73 (dd, \( J = 8.2, 2.4 \) Hz, 2H, H\(^4\) of C\(_6\)H\(_4\)OR), 6.55, 6.51 (each d, \( J = 12.4 \) Hz, 4H, CH=CH), 3.81 (t, \( J = 6.6 \) Hz, 4H, OCH\(_2\)), 1.74–1.66 (m, 4H, CH\(_2\)), 1.44–1.22 (several m, 20H,
Chapter 2

CH₂), 0.92–0.86 (m, 6H, CH₃). ¹³C {¹H} NMR (CDCl₃): δ 159.0 (s, C³ of C₆H₄OR), 138.6 (s, C¹ of Ar), 136.0 (s, C¹ of p-phenylene), 130.2, 130.0 (each s, CH=CH), 129.1 (s, C⁵ of C₆H₄OR), 128.8 (s, C²,³,⁵,⁶ of p-phenylene), 121.3 (s, C⁶ of C₆H₄OR), 114.5, 113.8 (each s, C² and C⁴ of C₆H₄OR), 67.8 (s, OCH₂), 31.8, 29.3, 29.2, 29.2, 26.0, 22.7 (each s, CH₂), 14.1 (s, CH₃). Anal. Calcd. for C₃₈H₅₀O₂: C, 84.71; H, 9.35. Found: C, 84.43; H, 9.36.

(Z,Z)-5. Pale yellow oil. ¹H NMR (CDCl₃): δ 7.45, 7.31 (each d, J = 8.2 Hz, 8H, C₁₂H₈), 7.13 (t, J = 7.8 Hz, H² of C₆H₄OR), 6.86 (d, J = 7.6 Hz, 2H, H⁶ of C₆H₄OR), 6.82 (s, 2H, H₂ of C₆H₄OR), 6.75 (dd, J = 8.2, 2.4 Hz, 2H, H⁴ of C₆H₄OR), 6.59 (s, 4H, CH=CH), 3.80 (t, J = 6.6 Hz, 4H, OCH₂), 1.73–1.64 (m, 4H, CH₂), 1.42–1.19 (several m, 20H, CH₂), 0.91–0.84 (m, 6H, CH₃). ¹³C {¹H} NMR (CDCl₃): δ 159.0 (s, C³ of C₆H₄OR), 139.2, (s, C₁₂H₈) 138.5 (s, C¹ of C₆H₄OR), 136.2 (s, C₁₂H₈), 130.4, 129.8 (each s, CH=CH), 129.8 (s, C₁₂H₈), 129.2 (s, C⁵ of C₆H₄OR), 126.5 (s, C₁₂H₈), 121.2 (s, C⁶ of C₆H₄OR), 114.4, 113.8 (each s, C² and C⁴ of C₆H₄OR), 67.8 (s, OCH₂), 31.8, 29.3, 29.2, 29.2, 26.0, 22.6 (each s, CH₂), 14.1 (s, CH₃). Anal. Calcd. for C₄₄H₅₄O₂: C, 85.94; H, 8.85. Found: C, 85.87; H, 8.87.

(f) (E,E)-Bis(3-octyloxystyryl)arenes ((E,E)-4 and 5).

\[
\begin{align*}
\text{R}_3\text{Si} & \quad \text{Ar} \quad \text{SiR}_3 \\
\text{(E,E)}-8b,c & \quad + \quad \text{OC}_6\text{H}_{17} \\
\text{[Pd(µ-Cl)(η³-allyl)]}_2 & \quad \text{Bu}_4\text{NF} \\
\text{THF} & \quad \text{→} \\
\text{(E,E)-4,5} & \quad \text{((E,E)/(Z) > 99/1)}
\end{align*}
\]

A typical procedure is reported for (E,E)-4. To a solution of (E,E)-8b ((E)/(Z) > 99/1) (268 mg, 0.400 mmol) and 19 (292 mg, 0.880 mmol) in THF (4 mL) were added [Pd(µ-Cl)(η³-allyl)]₂ (14.6 mg, 40.0 µmol) and 1.0 M solution of Bu₄NF·3H₂O in THF (0.80 mL, 0.80 mmol). The mixture was stirred at room temperature for 72 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO₂, hexane/CH₂Cl₂ (4/1)), giving (E,E)-4 ((E,E) > 99%) as a white solid (109 mg, 52% yield). (E,E)-5 was similarly synthesized using (E,E)-8c ((E,E) > 99%) in 51% yield.
All-cis and All-trans Poly(m-phenylenevinylene)s

(E,E)-4. Pale yellow solid. Mp: 112 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.50 (s, 4H, \(p\)-phenylene), 7.26 (t, \(J = 7.9\) Hz, 2H, H\(^5\) of Ar), 7.12–7.08 (m, 6H, H\(^6\) of Ar and 2 \(\times\) CH=CH), 7.06 (s, 2H, H\(^2\) of Ar), 6.81 (dd, \(J = 7.8, 2.0\) Hz, 2H, H\(^4\) of Ar), 4.00 (t, \(J = 6.6\) Hz, 4H, OCH\(_2\)), 1.85–1.76 (m, 4H, CH\(_2\)), 1.52–1.25 (several m, 20H, CH\(_2\)), 0.93–0.87 (m, 6H, CH\(_3\)). \(^{13}\)C\({^1\)H}\)NMR (CDCl\(_3\)): \(\delta\) 159.5 (s, C\(^3\) of Ar), 138.7 (s, C\(^1\) of Ar), 136.7 (s, C\(^{1,4}\) of \(p\)-phenylene), 129.6 (s, C\(^5\) of Ar), 128.6, 128.5 (each s, CH=CH), 126.9 (s, C\(^{2,3,5,6}\) of \(p\)-phenylene), 119.1 (s, C\(^d\) of Ar), 113.9, 112.3 (each s, C\(^2\) and C\(^6\) of Ar), 68.0 (s, OCH\(_2\)), 31.8, 29.4, 29.3, 26.1, 22.7 (each s, CH\(_2\)), 14.1 (s, CH\(_3\)). Anal. Calcd. for C\(_{38}\)H\(_{50}\)O\(_2\): C, 84.71; H, 9.35. Found: C, 84.45; H, 9.19.

(E,E)-5. Pale yellow solid. Mp: 182 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.64, 7.59 (each d, \(J = 8.4\) Hz, 8H, C\(_{12}\)H\(_8\)), 7.27 (t, \(J = 7.9\) Hz, 2H, H\(^5\) of Ar), 7.15–7.10 (m, 6H, H\(^6\) of Ar and 2 \(\times\) CH=CH), 7.08 (s, 2H, H\(^2\) of Ar), 6.82 (dd, \(J = 8.1, 2.3\) Hz, 2H, H\(^4\) of Ar), 4.01 (t, \(J = 6.6\) Hz, 4H, OCH\(_2\)), 1.86–1.77 (m, 4H, CH\(_2\)), 1.53–1.25 (several m, 20H, CH\(_2\)), 0.93–0.87 (m, 6H, CH\(_3\)). \(^{13}\)C\({^1\)H}\)NMR (CDCl\(_3\)): \(\delta\) 159.5 (s, C\(^3\) of Ar), 139.8 (s, C\(_{12}\)H\(_8\)), 138.7 (s, C\(^1\) of Ar), 136.4 (s, C\(_{12}\)H\(_8\)), 129.6 (s, C\(^5\) of Ar), 128.8, 128.4 (each s, CH=CH), 127.1, 127.0 (each s, C\(_{12}\)H\(_8\)), 119.2 (s, C\(^d\) of Ar), 113.9, 112.4 (each s, C\(^2\) and C\(^6\) of Ar), 68.0 (s, OCH\(_2\)), 31.9, 29.4, 29.3, 26.1, 22.7 (each s, CH\(_2\)), 14.1 (s, CH\(_3\)). Anal. Calcd. for C\(_{44}\)H\(_{54}\)O\(_2\): C, 85.94; H, 8.85. Found: C, 85.52; H, 8.86.

Photoisomerization in Solution. A sample solution in benzene (4 mg L\(^{-1}\)) was prepared in a quartz cell. Nitrogen gas was bubbled through the solution at room temperature for 5 min. The sample was irradiated with a Xe lamp (\(\lambda_{max} = 365\) nm, 0.87 mW cm\(^{-2}\)), and the photoisomerization was monitored by UV-vis absorption spectroscopy.

Photoisomerization of PmPVs in Thin Films. A solution of PmPV in CHCl\(_3\) (2.0 wt\%) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 \(\mu\)m, Hydrophobic; ADVANTEC). A thin film of PmPV was prepared by spin-coating on a quartz plate (1 cm\(^2\)); the filtrate (50 \(\mu\)L) was dropped on a plate, and the plate was accelerated to 1200 rpm rotation for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. After dried under...
vacuum at room temperature for 30 min, the film was placed in a quartz cell under a nitrogen atmosphere, and analyzed by UV-vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, irradiated by a Xe lamp ($\lambda_{\text{max}} = 365$ nm, $21.0$ mW cm$^{-2}$), and the photoisomerization was monitored by UV-vis absorption spectroscopy. The photo-irradiated 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.

References and Notes


All-cis and All-trans Poly(m-phenylenevinylene)s


(8)  The OCH$_2$ proton signals appear at around δ 3.6 and 4.0 for cis and trans isomers, respectively. The upfield shifts observed for cis isomers are due to the shielding effects of arylene rings as previously reported.$^{1a,1b,7}$

(9)  The small signal observed at 3.84–3.70 for all-cis 1a ((a) in Figure 1A) was assigned to the OCH$_2$ protons of terminal C$_6$H$_4$OC$_8$H$_{17}$ group, formed by hydrolysis of benzeneboronic acid ester; the chemical shift was in accordance with that of (Z)-2 (δ 3.77).


Chapter 3

Reaction of \textit{trans}-[Pd(CH=CHPh)Br(PMePh\textsubscript{2})\textsubscript{2}] with Styryl Bromide Affording 1,4-Diphenylbutadiene.

An Unexpected Homo-Coupling Process Induced by P–C Reductive Elimination

Abstract

Reaction of (Z)-styryl bromide (1) with PhB(OH)\textsubscript{2} in toluene at 80 °C for 1 h in the presence of [Pd(PPh\textsubscript{3})\textsubscript{4}] (1.5 mol%) and an aqueous solution of K\textsubscript{2}CO\textsubscript{3} (3 equiv) affords (Z)-stilbene as the cross-coupling product in 99% yield. On the other hand, the same reaction of the (E)-isomer of 1 forms considerable amounts of homo-coupling products (1,4-diphenylbutadiene (2, 22%) and biphenyl (27%)) in addition to the cross-coupling product ((E)-stilbene, 73%). The formation of 2 was examined by kinetic experiments using \textit{trans}-[[Pd\{CH=CHPh-(E)\}Br(PMePh\textsubscript{2})\textsubscript{2}]] ((E)-3) as a model of the presumed intermediate. Complex (E)-3 reacts with (E)-1 at 50 °C for 5 h, giving 2 (91%) and \textit{trans}-[[PdBr\textsubscript{2}(PMePh\textsubscript{2})\textsubscript{2}]] (4, 92%), together with a small amount of [Pd\{η\textsuperscript{2}-PhCH=CHPMePh\textsubscript{2}\}Br(PMePh\textsubscript{2})] (5, 8%). The reaction rate shows first-order dependence on the concentration of (E)-3 and 5, respectively, but is independent of the concentration of (E)-1. A novel homo-coupling process induced by P–C reductive elimination from (E)-3 giving 5 is proposed.
**Introduction**

As shown in Chapter 1, Suzuki–Miyaura-type polycondensation of (Z,Z)-1,4-bis-(2-bromoethenyl)benzene with 2,5-dioctyloxybenzene-1,4-diboronic acid cleanly forms all-cis poly(\(p\)-phenylenevinylene) (PpPV), which undergoes photo-induced insolubilization in thin films. It has been found that a 2-bromoethenyl group at the polymer end facilitates the photo-induced insolubilization to a notable extent. For further investigation of this phenomenon, the author has tried to synthesize all-trans PpPV bearing a 2-bromoethenyl group by Suzuki–Miyaura-type polycondensation, but (E,E)-1,4-bis (2-bromoethenyl)benzene has been found to provide a polymer containing a notable amount of butadiene unit in the main chain, resulting from the homo-coupling of alkenyl bromide. Therefore, the author has considered that the mechanistic information about the homo-coupling process should be essential for achieving a highly selective synthesis of all-trans PpPV without structural defects.

Scheme 1 illustrates a schematic view of homo-coupling processes previously reported. The first step is oxidative addition of organic halides (R–X) to low-valent transition metal species \([ML_n]\) (step a). The resulting \([MR(X)L_n]\) may undergo two reaction processes (A and B) affording homo-coupling products (R–R). Process A involves metathesis of \([MR(X)L_n]\) to give \([MR_2L_n]\) and \([MX_2L_n]\) (step b). The former forms R–R on reductive elimination (step c), whereas the latter is reduced to \([ML_n]\) when the reaction is conducted in catalytic systems containing reducing agents such as zinc and organometallic reagents (step d). This type of process was first documented by Tsou and Kochi for a nickel system using aryl bromides (Ar–Br) as substrates, where intermolecular exchange of aryl and bromo ligands between diamagnetic \([\text{Ni}^{II}\text{Br}(\text{Ar})(\text{PET}_3)_n]\) and paramagnetic \([\text{Ni}^{III}\text{Br}_2(\text{Ar})(\text{PET}_3)_n]\) was postulated to afford \([\text{Ni}^{III}(\text{Br})\text{Ar}_2(\text{PET}_3)_n]\) and \([\text{Ni}^{II}\text{Br}_2(\text{PET}_3)_n]\). More recently, Osakada and Yamamoto examined metathesis of diamagnetic \([\text{MAr}(X)(\text{bipy})]\) complexes (M = Ni, Pd; bipy = 2,2'-bipyridine) in detail and demonstrated high reactivity of cationic \([\text{MAr}(\text{bipy})]^+\) species.
On the other hand, process B involves oxidative addition of \( R-X \) to paramagnetic \( M^{III}RL_n \) or anionic \( [MRL_n]^- \) species generated by chemical or electrochemical reduction of \( [MR(X)L_n] \) (step e \( \rightarrow \) step f).\(^{11}\) The reaction forms \( [M^{III}R_2(X)L_n] \) or \( [MR_2L_n] \), which reductively eliminates \( R-R \) (step g). This type of process was originally proposed for nickel-catalyzed reactions by Colon and Kelsey\(^{11}\) and expanded to palladium-catalyzed systems by Amatore and Jutand.\(^{12}\)

This chapter deals with the homo-coupling process of styryl bromide (1) promoted by palladium(0) phosphine complexes. The author has attempted to clarify the following points using a model reaction of isolated \( \text{trans-}[\text{Pd(CH=CHPh)}\text{Br(PMePh}_2\text{)}_2] \) (3)\(^{13}\) with styryl bromide to give 1,4-diphenylbutadiene: (i) the effect of \( (E)/(Z) \) configuration of the styryl group; (ii) the mechanism of the homo-coupling process. It has been found that the butadiene formation proceeds via a novel homo-coupling process induced by P–C reductive elimination from 3 to give \( [\text{Pd(}\eta^2\text{-PhCH=CHPMePh}_2\text{)}\text{Br(PMePh}_2\text{)}] \) (5).\(^{14}\)
Results

Effect of (E)/(Z) Configuration of the Styryl Group. Cross-coupling reactions of (Z)- and (E)-styryl bromides (1) with PhB(OH)₂ were examined under the catalytic conditions for PPV synthesis. Thus, a 1:1 mixture of 1 and PhB(OH)₂ was heated at 80 °C for 1 h in toluene in the presence of [Pd(PPh₃)₄] (1.5 mol%) and an aqueous solution of K₂CO₃ (3 equiv). In agreement with the polymerization results, (Z)-1 selectively underwent cross-coupling giving (Z)-stilbene in quantitative yield (eq 1). On the other hand, the reaction of (E)-1 afforded considerable amounts of homo-coupling products (i.e., 1,4-diphenylbutadiene (2, 22%) and biphenyl (27%)), along with (E)-stilbene as the cross-coupling product (73%) (eq 2). It should be noted that butadiene 2 contains a significant amount of (E,Z)-isomer in addition to the (E,E)-isomer that is expected from the geometry of starting (E)-1. Since the cross-coupling product retains totally the original (E) configuration, it is likely that the (E)/(Z) isomerization of styryl group takes place uniquely in the homo-coupling process.

Next, the author examined the homo-coupling reaction giving 2 in stoichiometric systems using trans-[Pd(CH=CHPh)Br(PMePh₂)₂] (3) bearing (Z)- and (E)-styryl groups. While the PMePh₂ complexes were employed instead of the PPh₃ analogues for solubility
reason, their reactions with styryl bromides faithfully reproduced the characteristic points observed in the catalytic systems. Thus, (Z)-3 was almost unreactive to (Z)-styryl bromide ((Z)-1). On the other hand, (E)-3 smoothly reacted with (E)-styryl bromide ((E)-1, 20 equiv) in C₆D₆/CD₂Cl₂ (5/1) at 50 °C for 5 h to afford a geometrical mixture of 1,4-diphenylbutadiene (2, (E,E)/(E,Z) = 48/52, totally 91%), together with trans-[PdBr₂(PMePh₂)₂] (4, 92%) (eq 3). Accordingly, (i) much higher reactivity of (E)-styryl isomer than (Z)-styryl isomer towards homo-coupling, and (ii) the occurrence of (E)/(Z) isomerization of styryl group during the homo-coupling process were evidenced in the stoichiometric systems as well. As described below, the remaining part of (E)-3 (8%) is converted to styrylphosphonium complex 5, which is formed by P–C reductive elimination of styryl and PMePh₂ ligands.

\[
\begin{align*}
\text{(E)-3} & \quad \text{Pd-Br} \quad \text{PMePh₂} \\
+ \quad \text{(E)-1} & \quad \text{Pd-Br} \quad \text{PMePh₂} \\
\text{C₆D₆/CD₂Cl₂ (5/1)} & \quad \text{50 °C, 5 h} \\
\text{Ph} & \quad \text{Br} \\
\text{2} & \quad 91\% \\
\text{[(E,E)/(E,Z) = 48/52]} & \quad \text{4} & \quad 92\% \\
\text{5} & \quad 8\% \\
\end{align*}
\]

**Kinetic Examination of the Homo-Coupling Mechanism.** Figure 1 shows the time-course of eq 3. Palladium dibromide 4 forms at the expense of (E)-3. At the same time, complex 5 increases, while this complex is converted at the final stage to the other palladium species [Pd{CH=CHPh-(E)}{(µ-Br)(PMePh₂)}₂] (6) with liberation of [PhCH=CHPMePh₂]⁺Br⁻ (7). It was confirmed that the amount of butadiene 2 is consistent with that of 4 through the reaction. Clearly, the reaction curves for the conversion of (E)-3 and the formation of 4 are S-shaped, showing the occurrence of an autocatalytic process. Since the reaction is apparently accelerated as the amount of 5 increases, we next investigated the reaction of (E)-3 with (E)-1 in the presence of added 5. Complex 5 was prepared separately according to the procedure reported for PPh₃ analogues.
Figure 1. The time-course of the reaction of (E)-3 (50 mM) with (E)-1 (1.0 M) in C₆D₆/CD₂Cl₂ (5/1 = v/v) at 50 °C.

Table 1 lists the first-order rate constants (k₁) thus obtained. The k₂ values in the fourth column are second-order rate constants estimated by applying kinetic data to the following equation: $\ln\{[(E)-3]₀/([(E)-3]₀ - [4]₀)\} = k₂([5]₀ \times t)$. Thus, since the gradual formation of 5 from (E)-3 could not be ignored even in the presence of added 5, the formation rate of 4 was compensated for the concentration of 5 at time t. This treatment resulted in good linear correlations for all runs up to 83% conversion of (E)-3, giving almost identical k₂ values ($2.4(1) \times 10^{-2} \text{ s}^{-1} \text{ M}^{-1}$) (Figure 3). Hence the first-order dependence of the reaction rate on the concentration of (E)-3 and 5, respectively, was confirmed: $d[4]/dt = k₂[(E)-3][5]$. 

Figure 2 shows the time-course in the presence of added 5, where the amounts of 4 and 5 are based on the amount of (E)-3 initially employed ([((E)-3]₀ = 50 mM). Both the yield and the formation rate of 4 are enhanced by addition of 5 to the system ([5]₀ = 5–15 mM, runs 1–3). Furthermore, the amount of 5 generated from (E)-3 during the reaction clearly decreases as the amount of added 5 increases. It should be noted that the time-yield curves for 4 have a simple form (not S-shaped). Actually, the reactions obeyed the first-order kinetics up to 63% conversion of (E)-3.
Figure 2. The time-course of the reaction of (E)-3 (50 mM) with (E)-1 (1.0 M) in C₆D₆/CD₂Cl₂ (5/1 = v/v) at 50 °C in the presence of isolated 5.

Table 1. Kinetic Data for Formation of 4 in the Reactions of (E)-3 and (E)-1

<table>
<thead>
<tr>
<th>run</th>
<th>[5]₀ (mM)</th>
<th>10⁴k₁ (s⁻¹)</th>
<th>10²k₂ (s⁻¹ M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>—</td>
<td>2.5(1)</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1.80(2)</td>
<td>2.37(2)</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2.72(2)</td>
<td>2.36(2)</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>3.86(6)</td>
<td>2.54(4)</td>
</tr>
</tbody>
</table>

aReaction conditions: [(E)-3]₀ = 50 mM, [(E)-1]₀ = 1.0 M, in C₆D₆/CD₂Cl₂ (5/1 = v/v), at 50 °C. bEstimated by regression analysis of the kinetic data (up to 63% conversion of (E)-3) using the following equation: ln{[(E)-3]₀/[(E)-3]₀ – [4]₀)} = k₁t. cEstimated by regression analysis of the kinetic data (up to 83% conversion of (E)-3) using the following equation: ln{[(E)-3]₀/[(E)-3]₀ – [4]₀)} = k₂([5]₀ × t). dThe data for Figure 1. eData for less than 20% conversion of (E)-3 were omitted from the calculation because the concentration of 5 was too low to be accurately analyzed (<3%).
Table 2 compares half-lives of (E)-3 under various conditions. The reaction is highly sensitive to solvent polarity and clearly faster in a polar solvent (runs 1–3; runs 4–5). On the other hand, the reaction rate is less sensitive to the concentration of (E)-styryl bromide ((E)-1) (runs 1 and 4; runs 2 and 5). Although small variations of half-lives are observed depending on the concentration of (E)-1, they are attributable to the change in polarity of reaction media. Thus, in C₆D₆ as a nonpolar solvent, the reaction is faster at higher concentration of (E)-1, because (E)-1 possesses higher polarity than benzene (run 1 > run 4). To the contrary, the higher concentration of (E)-1 makes the reaction slower when the reaction solution contains CD₂Cl₂ as a highly polar solvent (run 2 < run 5). Accordingly, it is concluded that the rate of homo-coupling (i.e. the formation of butadiene 2) is essentially independent of the concentration of (E)-styryl bromide ((E)-1). As seen from runs 6 and 7, the reaction is retarded by free PMePh₂ and [PhCH=CHPMePh₂]⁺Br⁻ (7), respectively, while the effect of 7 is small.
Table 2. Half-Lives of (E)-3 in Reactions with (E)-1*

<table>
<thead>
<tr>
<th>run</th>
<th>[(E)-1]₀ (M)</th>
<th>solvent</th>
<th>additive</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>C₆D₆</td>
<td>—</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>C₆D₆/CD₂Cl₂ (5/1)</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>C₆D₆/CD₂Cl₂ (1/1)</td>
<td>—</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>C₆D₆</td>
<td>—</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>C₆D₆/CD₂Cl₂ (5/1)</td>
<td>—</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>C₆D₆/CD₂Cl₂ (5/1)</td>
<td>PMePh₂ (5 mM)</td>
<td>280</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>C₆D₆/CD₂Cl₂ (5/1)</td>
<td>7 (1.5 mM)ᵇ</td>
<td>130</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: [(E)-3]₀ = 50 mM, at 50 °C. *ᵇ* 7: [PhCH=CHPMePh₂]⁺Br⁻.

**Labeling Experiment.** The kinetic experiments revealed a crucial role of styrylphosphonium complex 5 in the homo-coupling process. In this connection, the reaction of (E)-3 with (E)-1 was examined in the presence of [Pd{η²-(E)-m-MeC₆H₄CH=CH-PMePh₂}Br(PMePh₂)] (5a, 0.2 equiv, 10 mM) in place of 5. As shown in eq 4, the reaction gave 1,4-diphenylbutadiene 2 and palladium dibromide 4 in almost quantitative yields. Thus, the m-MeC₆H₄CH=CH group of 5a was not incorporated into the product.

\[
\begin{align*}
\text{(E)-3} + \text{(E)-1} + & \quad \text{m-tolyl} \\
(20 \text{ equiv}) + & \quad \text{Ph₂MeP} \\
\text{5a} (0.2 \text{ equiv}) & \quad \text{Pd}^+ \\
\text{C₆D₆/CD₂Cl₂ (5/1)} & \quad \text{50 °C, 2 h}
\end{align*}
\]

Not observed
Relation between Stoichiometric and Catalytic Reactions. The reaction of styryl complex \((E)-3\) with \((E)\)-styryl bromide \(((E)-1)\) afforded butadiene \(2\) and palladium dibromide \(4\) in over 90% yields (eq 3). When this reaction proceeds catalytically, \(4\) should be reduced to a Pd(0) species, which subsequently undergoes oxidative addition of \((E)-1\) to reproduce \((E)-3\). Since the catalytic reaction in eq 2 formed a comparable amount of biphenyl along with \(2\), it is likely that \(\text{PhB(OH)}_2\) serves as a reducing agent in conjunction with a base. In fact, complex \(4\) smoothly reacted with \(\text{PhB(OH)}_2\) (3 equiv) in toluene in the presence of an aqueous solution of \(\text{K}_2\text{CO}_3\) (9 equiv) (eq 5). The reaction was completed in 30 min at 50 °C to give biphenyl in 90% yield. Similarly, the \(\text{PPh}_3\) complex \(4a\) formed a quantitative yield of biphenyl in 10 min. The observed reactivity of \(4a\) was high enough to be operative as an elementary process in the catalytic conversion of \((E)-1\).

\[
\begin{align*}
\text{Br-Pd-Br} & \quad \text{aq K}_2\text{CO}_3 \\
4 \quad \text{(L = PMePh}_2\text{)} & \quad \text{toluene, 50 °C} \\
\text{PhB(OH)}_2 \quad \text{(3 equiv)} & \quad \text{Ph-Ph} + [\text{PdL}_2] \\
4a \quad \text{(L = PPh}_3\text{)} & \quad 30 \text{ min} \\
& \quad 10 \text{ min} \quad 90\% \\
& \quad 100\%
\end{align*}
\]

Discussion

The following points have emerged from the experimental results. (1) \((Z)\)-styryl bromide \(((Z)-1)\) is much less reactive than the corresponding \((E)\)-isomer \(((E)-1)\) toward dehalogenative homo-coupling giving 1,4-diphenylbutadiene \(2\), because the \((Z)\)-styrylpalladium intermediate \(((Z)-3)\) is sufficiently stable toward P–C reductive elimination. (2) In contrast, \((E)\)-styrylpalladium \(((E)-3)\) readily undergoes P–C reductive elimination to give styrylphosphonium complex \(5\), which induces the reaction of \((E)-3\) with \((E)-1\) to afford \(2\) and palladium dibromide \(4\). (3) The homo-coupling reaction involves \((E)/(Z)\) isomerization of the styryl group to give a mixture of \((E,E)\)- and \((E,Z)\)-isomers of \(2\). (4) The rate of formation of \(2\) and \(4\) shows first-order dependence on the concentration of
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(E)-3 and 5, respectively, but is independent of the concentration of (E)-1. 5 A polar solvent accelerates the reaction, whereas free PMePh2 and [PhCH=CHPMePh2]Br− (7) retard the reaction. 6 The styryl group of styrylphosphonium complex 5 is not incorporated into the homo-coupling product 2. 7 Palladium dibromide (4 or 4a) is readily reacts with PhB(OH)2 in the presence of aqueous K2CO3 to afford biphenyl and a Pd(0) species.

Taking these observations into account, the author proposes the mechanism in Scheme 2 for the conversion of (E)-1 and (E)-3 into 2 and 4, which consists of initiation (steps a, b) and production (steps c, d) processes. First, styryl complex (E)-3 undergoes P–C reductive elimination to give styrylphosphonium complex 5 (step a). Unlike the arylpalladium analogues ([PdAr1(X)(PAR3)2]; Ar1, Ar2 = Ph, p-tolyl, etc.),19 the P–C coupling proceeds irreversibly, as confirmed by the labeling experiment in eq 4. Complex 5 then reacts with styryl bromide ((E)-1) to afford a three-coordinated complex A with liberation of [PhCH=CHPMePh2]Br− (7) (step b).20

Scheme 2
Complex A serves as a key intermediate in the production process. Intermolecular exchange of the styryl ligand in A and the bromo ligand in \((E)-3\) forms bis(styryl) complex B and dibromo complex 4 (step c). Reductive elimination of 2 from B, followed by oxidative addition of \((E)-1\) to a resulting Pd(0) species, regenerates A (step d). Accordingly, A catalyzes the conversion of \((E)-1\) and \((E)-3\) into 2 and 4. In this case, since the reaction rate is independent of the concentration of \((E)-1\), step d must be much faster than step c. This situation is very convincing because the C–C reductive elimination from related cis-[Pd(CH=CHPh)(Me)(PMePh₂)₂] and the oxidative addition of \((E)\)-styryl bromide to a Pd(0) phosphine complex proceed readily even at room temperature. ¹³,²¹

The reaction rate showed first-order dependence on the concentration of \((E)-3\) and 5, respectively. Apart from \((E)-3\) as the substrate of step c, the kinetic relation of 5 to the production process deserves discussion. It is assumed that 5 is converted to A and 7 by reaction with \((E)-1\). In fact, 7 is generated in the system at the final reaction stage, along with 6 as a dimer of A (Figure 1). However, since 6 and 7 are not observed in the early to middle stage of the reaction, it must be considered that 5 and A are rapidly interconverted, and the equilibrium lies far on the side of 5. ²² In this situation, complex 5 remains apparently unchanged in the reaction system, because A is recycled as catalyst in the production process and therefore its concentration is maintained. On the other hand, when \((E)-3\) is almost completely consumed at the final stage, A is dimerized to a stable form, to be converted entirely to 6 and 7.

The 1,4-diphenylbutadiene (2) was obtained as a mixture of \((E,E)\)- and \((E,Z)\)-isomers. Since \((Z)\)-styryl complex \((Z)-3\) was not observed in the system during the reaction, the \((E)/(Z)\) isomerization of the styryl group should be operative in step c in Scheme 2, causing intermolecular exchange of the styryl ligand in \((E)-3\) and the bromo ligand in A. Scheme 3 illustrates a plausible mechanism responsible for this phenomenon. The first step is very probably \(\eta^2\)-coordination of the styryl ligand of \((E)-3\) to the vacant coordination site of A. The styryl ligand then changes its coordination to an \(\eta^1\)-fashion, in conjunction with the transfer of bromo ligand in least motion. This change in coordination mode of the styryl
ligand provides intermediate D involving a contribution of the canonical structure given in Scheme 3, in which free rotation of the μ-styryl ligand is possible. Accordingly, the two geometrical isomers of 2 are formed.

Conclusions

The author has demonstrated a novel homo-coupling process of (E)-styryl bromide promoted by palladium(0) phosphine complexes. Thus, the reaction of (E)-styryl complex ((E)-3) with (E)-styryl bromide ((E)-1) is promoted by a catalytic amount of coordinatively unsaturated complex A, which is generated by P–C reductive elimination of the styryl and
PMePh$_2$ ligands from ($E$)-3, followed by oxidative addition of ($E$)-1 to resulting styrylphosphonium complex 5. The author has also shown that ($E$)/($Z$) isomerization of the styryl group, which takes place during the formation of 1,4-diphenylbutadiene (2), is reasonably accounted for by a mechanism involving intermolecular exchange of the styryl ligand between A and ($E$)-3.

Dehalogenative homo-coupling catalyzed by palladium complexes has been examined mainly for the reactions with aryl halides as substrates. Process B in Scheme 1 is currently most accepted for such reactions, where oxidative addition of aryl halides to anionic [MRL$_n$]$^-$ intermediates formed by two-electron reduction of [MR(X)L$_n$] is considered. In contrast, the author found a considerably different type of process for the reaction of ($E$)-styryl bromide (($E$)-1) to give 1,4-diphenylbutadiene (2). The C–C coupling process proposed in Scheme 2 resembles previous observations of Ozawa and Yamamoto for the reactions of trans-[PdAr$_2$L$_2$] with R–X (R = Me, aryl; L = PEt$_2$Ph), where trans-[PdR(X)L$_2$] formed by oxidative addition of R–X to a palladium(0) species catalyzes the conversion of trans-[PdAr$_2$L$_2$] and R–X into Ar–R.

**Experimental Section**

**General Considerations.** All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Nitrogen and argon gas were dried by passing through P$_2$O$_5$ (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer ($^1$H NMR 400.13 MHz, $^{13}$C NMR 100.62 MHz, and $^{31}$P NMR 161.97 MHz). Chemical shifts are reported in $\delta$ (ppm), referenced to the $^1$H (residual protons), and $^{13}$C signals of deuterated solvents or to the $^{31}$P signal of an external 85% H$_3$PO$_4$ standard. Mass spectra were measured on a Shimadzu GC-MS QP2010 spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a CBP-1 capillary column (25 m $\times$ 0.25 mm). Melting points were measured with a Yanaco
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MP-S3 instrument. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). 

\[
\text{C}_6\text{D}_6 \text{ and CD}_2\text{Cl}_2 \text{ were dried over lithium aluminum hydride (for C}_6\text{D}_6 \text{) or calcium hydride (for CD}_2\text{Cl}_2 \text{), transferred under vacuum, and stored over activated molecular sieves (MS4A). Et}_2\text{O and CH}_2\text{Cl}_2 \text{ (Wako, dehydrated) were used as received.}
\]

\((E)\)-Styryl bromide \(((E)-1)\) was purified in an alkaline condition to remove contamination of the \((Z)\)-isomer.\(^{24}\) The following compounds were synthesized according to the literature:

\((Z)\)-styryl bromide \(((Z)-1)\),\(^{25}\) \([\text{Pd(PPh}_3\text{)}_4]\),\(^{26}\) \(\text{trans-[Pd}\{\text{CH=CH(PH-(Z)}\}\text{Br(PPMePh}_2\text{)}_2]\) \(((Z)-3)\),\(^{13a}\) \(\text{trans-[PdBr}_2\{\text{PPMePh}_2\text{)}_2]\) \((4)\),\(^{27}\) \(\text{trans-[PdBr}_2\{\text{PPh}_3\text{)}_2]\) \((4a)\),\(^{28}\) \([\eta^5\text{-C}_5\text{H}_5\eta^3\text{-C}_3\text{H}_5]\text{Pd]}\),\(^{29}\) \([\text{Pd(PPh}_2\text{)}_4]\),\(^{30}\) and \([\text{Pd(dba)}_2]\).\(^{31}\)

**Synthesis of** \(\text{trans-[Pd}\{\text{CH=CH(PH-(E)}\}\text{Br(PPMePh}_2\text{)}_2]\) \(((E)-3)\). \(\text{PMePh}_2\) (411 mg, 2.05 mmol) was added to a solution of \([\eta^5\text{-C}_5\text{H}_5\eta^3\text{-C}_3\text{H}_5]\text{Pd]}\) (213 mg, 1.00 mmol) in toluene (1.0 mL) at 0 °C. The mixture was stirred for 10 min, and \((E)-1\) (732 mg, 4.00 mmol) was added. The homogeneous solution was stirred at room temperature, causing gradual precipitation of a white solid. After 3 h, hexane (5 mL) was added, and the mixture was cooled to –20 °C. The white precipitate formed in the system was collected by filtration, washed successively with hexane (2 × 2 mL) and Et\(_2\)O (2 × 2 mL), and dried under vacuum. The crude product was purified by recrystallization from CH\(_2\)Cl\(_2\)/Et\(_2\)O at room temperature, washed with Et\(_2\)O, and dried under vacuum at 0 °C to afford pale brown crystals of the title compound (603 mg, 87% yield). The NMR data were identical with those reported.\(^{14b}\) \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\)): \(\delta 7.65–7.58 \text{ and 7.45–7.35} \text{ (m, 20H in total), 7.05 \text{ (m, 2H), 6.93 \text{ (m, 1H), 6.54} \text{ (tt, } 3J_{HH} = 16.0 \text{ Hz, } 3J_{HP} = 9.6 \text{ Hz, 1H), 6.47 \text{ (d, } 3J_{HH} = 7.3 \text{ Hz, 2H), 5.64 \text{ (dt, } 3J_{HH} = 16.0 \text{ Hz, } 4J_{HP} = 1.9 \text{ Hz, 1H), 2.07 \text{ (virtual triplet, } J = 3.3 \text{ Hz, 6H).} \}
\]

\(^{31}\text{P}{\text{\{}^1\text{H}\}}\) NMR (CD\(_2\)Cl\(_2\)): \(\delta 7.8 \text{ (s).}
\]

**Synthesis of \((E)\)-[PhCH=CHPMePh\(_2\)]\(^+\)Br\(^-\) \((7)\).** This compound was prepared by the procedure reported for \((E)\)-[PhCH=CHPPh\(_3\)]\(^+\)Br\(^-\).\(^{15c}\) A solution of \((E)-1\) (802 mg, 4.38 mmol)
and PMePh₂ (878 mg, 4.38 mmol) in toluene (22 mL) was stirred at 100 °C in the presence of [Pd(PMePh₂)₄] (199 mg, 0.219 mmol) for 24 h. The white precipitate formed in the system was collected by filtration, washed with hexane and Et₂O, and dried under vacuum (1.57 g, 94%). Mp: 181–183 °C. ¹H NMR (CDCl₃): δ 7.89–7.74, 7.70–7.65, and 7.51–7.37 (m, 17H in total), 3.06 (d, ²JHP = 13.7 Hz, 3H).

¹³C{¹H} NMR (CDCl₃): 154.9 (d, ³JPC = 5 Hz), 134.7 (d, ⁴JPC = 3 Hz), 133.6 (d, ²JPC = 20 Hz), 132.9 (d, ³JPC = 11 Hz), 131.9 (s), 130.2 (d, ²JPC = 13 Hz), 129.2 (s), 129.1 (s), 119.7 (d, ¹JPC = 90 Hz), 106.4 (d, ¹JPC = 89 Hz), 10.7 (d, ¹JPC = 59 Hz). ³¹P{¹H} NMR (CDCl₃): δ 19.6 (s). Anal. Calcd for C₂₁H₂₀BrP: C, 65.81; H, 5.26. Found: C, 65.58; H, 5.32.

(E)-[m-MeC₆H₄CH=CHPMePh₂]⁺Br⁻ (7a) was similarly prepared as a white powder by the reaction of (E)-m-methylstyryl bromide (312 mg, 1.58 mmol) and PMePh₂ (317 mg, 1.58 mmol) in toluene (8 mL) in the presence of [Pd(PMePh₂)₄] (71.8 mg, 79.1 µmol) (585 mg, 93%). Mp: 138–140 °C. ¹H NMR (CDCl₃): δ 7.88–7.76 and 7.72–7.55 (m, 13H in total), 7.40 (dd, ³JHP = 23.1 Hz, ³JHH = 17.4 Hz, 1H), 7.34–7.27 (m, 2H), 3.10 (d, ²JHP = 13.7 Hz, 3H), 2.38 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 155.2 (d, ³JPC = 4 Hz), 138.9 (s), 134.7 (d, ⁴JPC = 3 Hz), 133.5 (d, ²JPC = 20 Hz), 132.9 (d, ³JPC = 11 Hz), 132.8 (s), 130.2 (d, ³JPC = 20 Hz), 129.7 (s), 129.0, (s), 126.4 (s), 119.8 (d, ¹JPC = 90 Hz), 105.9 (d, ¹JPC = 89 Hz), 21.2 (s), 10.7 (d, ¹JPC = 59 Hz). ³¹P{¹H} NMR (CDCl₃): δ 19.6 (s). Anal. Calcd for C₂₂H₂₂BrP: C, 66.51; H, 5.58. Found: C, 66.62; H, 5.67.

Synthesis of [Pd(η²-(E)-PhCH=CHPMePh₂)Br(PMePh₂)] (5). To a solution of PMePh₂ (128 mg, 0.639 mmol) in CH₂Cl₂ (6.4 mL) were added [Pd(dba)₂] (368 mg, 0.639 mmol) and 7 (245 mg, 0.639 mmol). The solution was stirred at room temperature for 3 h and filtered through a Celite pad. The solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ (3 mL) and diluted with Et₂O (10 mL), and a green solid formed in the solution was removed by filtration. This operation was repeated three times to give a crude product (255 mg, 58% yield). Recrystallization from CH₂Cl₂/Et₂O at –30 °C gave yellow crystals of the title compound (224 mg, 51% yield). Mp: 126–128 °C (dec). ¹H NMR
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(CD$_2$Cl$_2$): δ 8.04–7.97, 7.75–7.42, 7.24–6.86, and 6.81–6.78 (m, 25H in total), 3.34 (ddd, $^2$J$_{HP}$ = 19.8 Hz, $^3$J$_{HH}$ = 10.7 Hz, $^3$J$_{HP}$ = 4.1 Hz, 1H), 3.12 (ddd, $^3$J$_{HH}$ = 14.0 Hz, $^3$J$_{HH}$ = 10.7 Hz, $^3$J$_{HP}$ = 8.2 Hz, 1H), 2.83 (d, $^2$J$_{HP}$ = 13.7 Hz, 3H), 1.50 (d, $^2$J$_{HP}$ = 6.2 Hz, 3H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 144.8 (d, $^3$J$_{PC}$ = 11 Hz), 139.3 (d, $^1$J$_{PC}$ = 28 Hz), 137.0 (d, $^1$J$_{PC}$ = 29 Hz), 134.9 (d, $^3$J$_{PC}$ = 10 Hz), 133.5 (s), 134.8 (s), 132.8 (d, $^2$J$_{PC}$ = 14 Hz), 132.6 (d, $^3$J$_{PC}$ = 10 Hz), 132.5 (d, $^2$J$_{PC}$ = 14 Hz), 129.9 (d, $^2$J$_{PC}$ = 11 Hz), 129.2 (s), 129.1 (d, $^2$J$_{PC}$ = 12 Hz), 128.9 (d, $^4$J$_{PC}$ = 1 Hz), 128.7 (s), 128.4 (d, $^2$J$_{PC}$ = 9 Hz), 128.2 (d, $^3$J$_{PC}$ = 9 Hz), 127.4 (dd, $^1$J$_{PC}$ = 73 Hz, $^4$J$_{PC}$ = 10 Hz), 125.7 (s), 124.9 (s), 124.9 (d, $^1$J$_{PC}$ = 93 Hz), 59.5 (d, $^2$J$_{PC}$ = 9 Hz), 28.3 (d, $^1$J$_{PC}$ = 81 Hz, $^2$J$_{PC}$ = 36 Hz), 14.6 (d, $^1$J$_{PC}$ = 19 Hz), 13.7 (d, $^1$J$_{PC}$ = 67 Hz). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): δ 18.9 (d, $^3$J$_{PP}$ = 7 Hz), 6.7 (d, $^3$J$_{PP}$ = 6 Hz). Anal. Calcd for C$_{34}$H$_{33}$BrPdP: C, 59.19; H, 4.82. Found: C, 59.05; H, 4.94.

[Pd($\eta^2$-(E)-m-MeC$_6$H$_4$CH=CHPMePh$_2$)Br(PMePh$_2$)] (5a) was similarly obtained as yellow crystals from [Pd(dba)$_2$] (130 mg, 0.225 mmol), 7a (89.5 mg, 0.225 mmol), and PMePh$_2$ (45.1 mg, 0.225 mmol) (25.1 mg, 16%). Mp: 124–126 °C (dec). $^1$H NMR (CD$_2$Cl$_2$): δ 8.04–7.96, 7.78–7.45, 7.26–7.08 and 7.00–6.90 (m, 20H in total), 6.88 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H), 6.81 (d, $^3$J$_{HH}$ = 7.5 Hz, 1H), 6.66 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H), 6.56 (s, 1H), 3.37 (ddd, $^2$J$_{HP}$ = 19.9 Hz, $^3$J$_{HH}$ = 10.7 Hz, $^3$J$_{HP}$ = 4.0 Hz, 1H), 3.11 (ddd, $^3$J$_{HP}$ = 14.3 Hz, $^3$J$_{HH}$ = 10.7 Hz, $^3$J$_{HP}$ = 8.2 Hz, 1H), 2.82 (d, $^2$J$_{HP}$ = 13.7 Hz, 3H), 2.11 (s, 3H), 1.51 (d, $^2$J$_{HP}$ = 6.2 Hz, 3H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 144.6 (d, $^3$J$_{PC}$ = 12 Hz), 139.5 (d, $^1$J$_{PC}$ = 28 Hz), 138.2 (s), 137.0 (d, $^1$J$_{PC}$ = 29 Hz), 134.9 (d, $^3$J$_{PC}$ = 10 Hz), 133.5 (br), 132.8 (d, $^2$J$_{PC}$ = 14 Hz), 132.5 (d, $^2$J$_{PC}$ = 14 Hz), 129.9 (d, $^3$J$_{PC}$ = 11 Hz), 129.2 (s), 129.1 (d, $^3$J$_{PC}$ = 13 Hz), 128.9 (s), 128.6 (s), 128.5 (d, $^3$J$_{PC}$ = 9 Hz), 128.2 (d, $^3$J$_{PC}$ = 9 Hz), 127.4 (dd, $^1$J$_{PC}$ = 73 Hz, $^4$J$_{PC}$ = 10 Hz), 126.5 (s), 125.7 (s), 124.8 (d, $^1$J$_{PC}$ = 93 Hz), 122.6 (s), 59.8 (d, $^2$J$_{PC}$ = 5 Hz), 28.2 (dd, $^1$J$_{PC}$ = 82 Hz, $^2$J$_{PC}$ = 36 Hz), 21.5 (s), 14.6 (d, $^1$J$_{PC}$ = 19 Hz), 13.7 (d, $^1$J$_{PC}$ = 66 Hz). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): δ 18.8 (d, $^3$J$_{PP}$ = 8 Hz), 6.7 (d, $^3$J$_{PP}$ = 6 Hz). Anal. Calcd for C$_{33}$H$_{33}$BrPdP: C, 59.72; H, 5.01. Found: C, 59.44; H, 5.00.
**Catalytic Reactions.** To a 10 mL Schlenk tube containing PhB(OH)$_2$ (48.8 mg, 0.400 mmol), [Pd(PPh$_3$)$_4$] (6.9 mg, 6.0 µmol), and hexamethylbenzene (32.5 mg, 0.200 mmol; internal standard) were added successively toluene (2 mL), an aqueous solution of potassium carbonate (3.0 M, 0.40 mL, 1.2 mmol), and 1 (73.2 mg, 0.400 mmol). The mixture was stirred at 80 °C for 1 h. The coupling products were identified by GC-MS using authentic samples and analyzed quantitatively by GLC.

**Kinetic Experiments.** A typical procedure is as follows. The compounds (E)-3 (20.7 mg, 0.030 mmol), (E)-1 (110 mg, 0.60 mmol), and 1,3,5-trimethoxybenzene (2.5 mg, 0.015 mmol; internal standard) were placed in an NMR sample tube and dissolved in C$_6$D$_6$/CD$_2$Cl$_2$ (5/1 = v/v) (total 0.6 mL) at room temperature under a nitrogen atmosphere. The sample tube was capped with a rubber septum and placed in an NMR probe controlled to 50.0 ± 0.1 °C. The reaction was followed at intervals by $^1$H NMR spectroscopy using the following marker signals: (E)-3 ($\delta$ 1.98, PMe), 4 ($\delta$ 2.08, PMe), 5 ($\delta$ 2.55, 1.64, PMe), 6 ($\delta$ 2.14, PMe), 7 ($\delta$ 2.73, PMe), (E,E)-2 ($\delta$ 6.51, vinylic H), (E,Z)-2 ($\delta$ 6.31, vinylic H), 1,3,5-trimethoxybenzene ($\delta$ 6.14, Ar). $^{31}$P{$^1$H} NMR spectrum measured after completion of the reaction exhibited three singlets assignable to 4 ($\delta$ 5.4), 6 ($\delta$ 15.2), and 7 ($\delta$ 19.3).

**Reaction of trans-[PdBr$_2$(PPh$_3$)$_2$] (4a) with PhB(OH)$_2$.** To a 10 mL Schlenk tube containing 4a (79.1 mg, 0.100 mmol), PhB(OH)$_2$ (36.6 mg, 0.300 mmol), and hexamethylbenzene (16.2 mg, 0.100 mmol; internal standard) were added successively toluene (1.0 mL) and an aqueous solution of potassium carbonate (3.0 M, 0.30 mL, 0.90 mmol). The mixture was stirred at 50 °C for 10 min and analyzed by GC-MS and GLC, showing the formation of biphenyl in quantitative yield. The reaction of 4 (trans/cis = 93/7) was similarly conducted.
References and Notes

(1) Dehalogenative homo-coupling of aryl and alkenyl halides promoted by nickel\textsuperscript{2} and palladium\textsuperscript{3} complexes is a useful means of C–C bond formation,\textsuperscript{4} especially for the synthesis of π-conjugated polymers.\textsuperscript{5} This reaction also takes place quite often as a side reaction of the catalytic cross-coupling of organic halides with organometallic reagents.\textsuperscript{6,7}


Chapter 3


(14) P–C reductive elimination giving alkenylphosphonium complexes has been reported: (a) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz’mina, L. G.; Struchkov, Y. T.; Kaverin, V. V.; Koneva, N. Y. *J. Organomet. Chem.* 1985, 288, 119–129. (b) Duan,
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(15) (a) Treatment of (Z)-3 with (Z)-1 (20 equiv) in C₆D₆/CD₂Cl₂ (5/1) at 50 °C for 5 h gave a small amount of *trans*-[PdBr₂(PMePh₂)₂] (4, ca. 2%), while most of (Z)-3 remained unreacted. GLC analysis revealed no formation of 1,4-diphenylbutadiene (2). (b) Complex (Z)-3 was stable at 50 °C for 5 h in C₆D₆ in the presence of (E)-1 (20 equiv).

(16) (a) Heating (E)-3 in C₆D₆ at 50 °C for 6 h resulted in the formation of 5 in 52% yield as confirmed by NMR spectroscopy. Also formed in the solution are butadiene 2 ((E,E)/(E,Z) = 48/52, 23%) and dibromopalladium 4 (8%). (b) Unlike (E)-3, (Z)-3 was stable in C₆D₆ at 50 °C for 6 h.

(17) Although 6 could not be isolated, it was assigned as [Pd{CH=CHPh-(E)}(μ-Br)(PMePh₂)]₂ based on the similarity of NMR data [¹H NMR: δ 2.14 (d, JHP = 11.4 Hz, PCH₃); ³¹P{¹H} NMR: δ 15.2 (s)] to related [PdR(μ-Cl)(PMePh₂)]₂ (R = Ph, CH₂Ph). Anderson, G. K. *Organometallics* 1983, *2*, 665–668.

(18) (a) The yield of 4 in each run of Figure 2 (%): 94 (run 1), 96 (run 2), 98 (run 3). (b) The maximum amount of 5 derived from (E)-3 (%): 6 (run 1), 4 (run 2), 2 (run 3). Complex 5 was converted to 6 and 7 at the final stage as described for Figure 1.


(22) A polar solvent increases the equilibrium concentration of A and 7, causing enhancement in the reaction rate. On the other hand, addition of 7 to the system decreases the concentration of A and reduces the reaction rate. The retardation effect of free PMePh2 may be attributed to several reasons. For example, intermediate A is very probably captured as (E)-3. Furthermore, since complex 5 is converted to \([\text{Pd}\{\eta^2-(E)-\text{PhCH=CHPMePh}_2\}(\text{PMePh}_2)_2]\)Br by the coordination of PMePh2, the formation of A is possibly hindered by increasing coordination stability of the styrylphosphonium ligand.


Chapter 4

Mechanism of P–C Reductive Elimination from 
trans-[Pd(CH=CHPh)Br(PMePh₂)₂]

Abstract

The (E)- and (Z)-styryl isomers of trans-[Pd(CH=CHPh)Br(PMePh₂)₂] (1a) and [Pd(η²-PhCH=CHPMePh₂)Br(PMePh₂)] (2a) were prepared, and their P–C reductive elimination (1a → 2a) and P–C oxidative addition (2a → 1a) behaviors were examined. Kinetics and thermodynamics of the reactions are strongly affected by E/Z configurations of styryl group and solvent polarity. Complex (E)-1a readily undergoes P–C reductive elimination in CD₂Cl₂ as a polar solvent in high selectivity. On the other hand, while the (Z)-isomer of 1a is unreactive toward reductive elimination, (Z)-2a undergoes P–C oxidative addition favorably in non-polar benzene. X-ray diffraction analysis and DFT calculations for 1a and 2a provided reasonable accounts for these reaction features. Kinetic examinations revealed two types of P–C reductive elimination processes, which involve pre-dissociation and association of PMePh₂ ligand, respectively.
Chapter 4

Introduction

Reductive elimination is a crucial elementary process, often serving as the product-forming step in many catalytic organic transformations.\(^1\) Besides classical reactions to afford C–H and C–C bonds, reductive elimination of a carbon–heteroatom bond has attracted considerable recent attention in connection with palladium-catalyzed synthesis of heteroatom compounds.\(^2\) While the C–N and C–O bond formations are of central importance in such chemistry, there has been a growing interest in P–C reductive elimination of hydrocarbyl and phosphine ligands from Pd(II) complexes.\(^3\)\(^–\)\(^7\) It has been documented that complexes of the formula \[ \text{[PdAr}(X)(\text{PAR'})_2] \] (Ar, Ar’ = aryl; X = halogen) undergo P–C reductive elimination to give arylphosphonium halides (\[\text{[PAR'}_3]^+X^-\]) and Pd(0) species.\(^3\) This reaction is usually reversible with P–C oxidative addition, and the overall process results in Ar/Ar’ exchange between palladium and phosphorus atoms.\(^8\) The P–C reductive elimination has also been postulated for catalytic formation of aryl-,\(^4\) alkenyl-,\(^5\) and alkyl-phosphoniums,\(^6\) and functionalized phosphines.\(^7\)

Most of the reductive elimination processes involve the coupling of two anionic ligands. In contrast, P–C reductive elimination causes the bond-formation between anionic and neutral ligands. Accordingly, it is expected that the reaction possesses rather unique mechanistic features, differing significantly from common reductive elimination processes. Although the reductive elimination of arylphosphonium from \[ \text{[PdAr}(X)(\text{PAR'})_2] \] type complexes has been suggested to involve prior dissociation of one of the phosphine ligand,\(^3a\)\(^–\)\(^c\) intimate information about the mechanism of P–C reductive elimination is still limited.\(^9\) This is probably due to the concurrent operation of P–C oxidative addition, which makes the reaction system complicated.

As shown in Chapter 3, the homo-coupling reaction of (E)-styryl bromide promoted by a palladium(0) phosphine complex is induced by P–C reductive elimination from \[ \text{[Pd}(\text{CH}═\text{CHPh})(\text{Br})(\text{PAR'})_2]\] as a catalytic intermediate. This chapter deals with the mechanism of P–C reductive elimination from \textit{trans}−[\text{Pd}(\text{CH}═\text{CHPh})\text{Br}(\text{PMePh}_2)_2] (1\text{a}) to
give \([\text{Pd} (\eta^2\text{-PhCH}=\text{CHPMePh}_2)\text{Br} (\text{PMePh}_2)]\) (2a) and \([\text{Pd} (\eta^2\text{-PhCH}=\text{CHPMePh}_2)-(\text{PMePh}_2)_2\text{Br}\) (3a). Unlike the reactions of arylpalladium complexes, the P–C reductive elimination of styryl complexes forms \(\eta^2\)-styrylphosphonium complexes as the products, which are sufficiently stable for isolation. Therefore, the reaction has been successfully investigated in detail by kinetic experiments. The author herein describes that P–C reductive elimination of 1a is strongly dependent on E/Z configurations of styryl ligand. It will be also shown that two types of reductive elimination processes are operative, depending on the amount of free PMePh\(_2\) in the system.
Results and Discussion

P–C Reductive Elimination and Oxidative Addition Reactions. \((E)\)-styryl complexes having three kinds of tertiary phosphine ligands \(((E)-\text{1a–c})\) were heated in solution, and the reaction systems were examined at intervals by \(^1\)H NMR spectroscopy (eq 1). The results are summarized in Table 1.

\[
\begin{align*}
\text{Ph} & \quad \text{PR}_3 \\
\text{Pd} & \quad \text{Br} \\
\text{PR}_3 & \quad \text{Ph} \\
\text{PR}_3 & \quad \text{Ph}
\end{align*}
\]

\((E)-\text{1a}: \text{PR}_3 = \text{PMePh}_2 \\
(E)-\text{1b}: \text{PR}_3 = \text{PPh}_3 \\
(E)-\text{1c}: \text{PR}_3 = \text{PMe}_3
\]

\[
\begin{align*}
\text{Ph} & \quad \text{PR}_3 \\
\text{Pd} & \quad \text{Br} \\
\text{R}_3\text{P} & \quad \text{Br} \\
\text{PR}_3 & \quad \text{Ph}
\end{align*}
\]

\((E)-\text{2a} \\
(E)-\text{2b} \\
(E)-\text{2c}
\]

Complex \((E)-\text{1a}\) bearing PMePh\(_2\) ligands readily underwent P–C reductive elimination in CD\(_2\)Cl\(_2\) at 40 °C to give the corresponding styrylphosphonium complex \(((E)-\text{2a})\) in 82% selectivity (run 1). The remaining part of \((E)-\text{1a}\) was converted to trans-[PdBr\(_2\)(PMePh\(_2\))]\(_2\) (5%) and some unidentified palladium species. The author already confirmed that the dibromo complex is afforded by disproportionation of \((E)-\text{1a}\), and its formation is inhibited by free PMePh\(_2\).\(^{11}\) Actually, in the presence of added PMePh\(_2\) (1 equiv/\(\text{1a}\)), the P–C reductive elimination proceeded in 97% selectivity (run 2), where the product styrylphosphonium complex was obtained as [Pd\(\{\eta^2\text{-PhCH=CHPMePh}_2\}\)(PMePh\(_2\))]Br \(((E)-\text{3a})\), instead of \((E)-\text{2a}\).\(^{12}\) The conversion of \((E)-\text{1a}\) was strongly affected by solvent polarity; the reaction decelerated significantly in THF and benzene, and the selectivity of \((E)-\text{2a}\) decreased (runs 3 and 4). The PPh\(_3\) complex \((E)-\text{1b}\) behaved similarly, while the reactivity was apparently higher than that of \((E)-\text{1a}\) (runs 5 and 6). On the other hand, the PMe\(_3\) complex \((E)-\text{1c}\) was much less reactive than \((E)-\text{1a}\) and \((E)-\text{1b}\) (run 7).
Table 1. P–C Reductive Elimination of trans-[Pd{CH=CH(−(E))}Br(PR_3)_2] ((E)-1)

<table>
<thead>
<tr>
<th>run</th>
<th>complex</th>
<th>solvent</th>
<th>additive (PR_3, mM)</th>
<th>temp (°C)</th>
<th>(t_{1/2}) (min)</th>
<th>selectivity of 2 (or 3) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(E)-1a</td>
<td>CD_2Cl_2</td>
<td>0</td>
<td>40</td>
<td>ca. 5</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>(E)-1a</td>
<td>CD_2Cl_2</td>
<td>50</td>
<td>40</td>
<td>168</td>
<td>97c</td>
</tr>
<tr>
<td>3</td>
<td>(E)-1a</td>
<td>THF-(d_8)</td>
<td>0</td>
<td>50</td>
<td>48</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>(E)-1a</td>
<td>C_6D_6</td>
<td>0</td>
<td>50</td>
<td>60</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>(E)-1b</td>
<td>CD_2Cl_2</td>
<td>0</td>
<td>40</td>
<td>&lt;4</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>(E)-1b</td>
<td>CD_2Cl_2</td>
<td>50</td>
<td>40</td>
<td>35</td>
<td>96d</td>
</tr>
<tr>
<td>7</td>
<td>(E)-1c</td>
<td>CD_2Cl_2</td>
<td>0</td>
<td>40</td>
<td>270</td>
<td>43e</td>
</tr>
</tbody>
</table>

\(^a\) \([1]_0 = 50 \text{ mM. All reactions were examined by } ^1\text{H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.}\) \(^b\) Half-lives of 1. \(^c\) The sum of [Pd{η\(^2\)-PhCH=CHPMePh\(_2\)}(PMePh\(_2\))_2]Br ((E)-3a) (96%) and (E)-[PhCH=CH-PMePh\(_2\)]Br^- (1%). \(^d\) The product was [Pd{η\(^2\)-(E)-PhCH=CHPPh\(_3\)}(PPPh\(_3\))_2]Br ((E)-3b). \(^e\) The selectivity at 58% conversion of (E)-1c.

Unlike the (E)-styryl complexes, the (Z)-isomer trans-[Pd{CH=CH(−(Z))}-Br(PMePh\(_2\))_2] ((Z)-1a) was stable toward P–C reductive elimination; no trace of [Pd{η\(^2\)-(Z)-PhCH=CHPMePh\(_2\)}Br(PMePh\(_2\))] ((Z)-2a) was formed at 50 °C for 6 h. On the contrary, (Z)-2a was found to undergo oxidative addition of styrylphosphonium ligand (eq 2, Table 2). Heating a C_6D_6 solution of isolated (Z)-2a at 40 °C for 8 h resulted in the formation of (Z)-1a in 46% selectivity, together with (E)-2a (33%) and other palladium complexes including trans-[PdBr\(_2\)(PMePh\(_2\))_2] (4%) (run 1). The formation of (Z)-1a was entirely suppressed by added PMePh\(_2\) (1 equiv/1a), while the Z-to-E isomerization of styrylphosphonium ligand giving (E)-2a continued to proceed at a comparable rate (run 2). The reaction rate and the selectivity of (Z)-1a decreased significantly in CD_2Cl_2 as a polar solvent (run 3).
Table 2. P–C Oxidative Addition of \([\text{Pd}\{\eta^2-(Z)\text{-PhCH=CHPMePh}_2\}\text{Br(PMePh}_2\text{)}\}] \((Z)-2a\)

<table>
<thead>
<tr>
<th>run</th>
<th>solvent</th>
<th>PMePh(_2) conversion of selectivity (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mM)</td>
<td>((Z)-2a) (%)</td>
<td>((Z)-1a)</td>
<td>((E)-2a)</td>
</tr>
<tr>
<td>1</td>
<td>C(_6)D(_6)</td>
<td>0</td>
<td>79</td>
<td>46</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>C(_6)D(_6)</td>
<td>10</td>
<td>90</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>CD(_2)Cl(_2)</td>
<td>0</td>
<td>27</td>
<td>12</td>
<td>73</td>
</tr>
</tbody>
</table>

\([Z\text{-}2a]\)\(_0\) = 10 mM. All reactions were run at 40 °C for 8 h.

X-Ray Structures of 1\(a\) and 2\(a\). It has been found that reductive elimination and oxidative addition reactions of P–C bonds are markedly affected by E/Z configurations of styryl group and solvent polarity. Since these reactions are essentially reverse processes, and the conversion of \((E)-1a\) to \((E)-2a\) and that of \((Z)-2a\) to \((Z)-1a\) are operative under similar conditions, it seems likely that the observed tendencies mainly reflect the difference in thermodynamic stability between \((E)\)- and \((Z)\)-isomers of 1\(a\) and 2\(a\). The author therefore examined their structures by X-ray diffraction analysis and DFT calculations.
Figure 1. X-ray structures of (E)-1a and (Z)-1a (one of the crystallographically independent molecules). The thermal ellipsoids are drawn at the 30% probability levels. Hydrogen atoms, except for the H(1) atom of (Z)-1a, are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows. (E)-1a: Pd–Br = 2.5324(8), Pd–P(1) = 2.3139(10), Pd–P(2) = 2.3121(10), Pd–C(1) = 2.007(2), C(1)–C(2) = 1.325(3), Br–Pd–P(1) = 94.15(2), Br–Pd–P(2) = 90.08(3), C(1)–Pd–P(1) = 88.32(7), C(1)–Pd–P(2) = 87.50(7), Pd–C(1)–C(2) = 128.85(18), C(1)–C(2)–C(3) = 123.4(2). (Z)-1a: Pd–Br = 2.5233(8), Pd–P(1) = 2.3187(12), Pd–P(2) = 2.3128(13), Pd–C(1) = 2.002(5), C(1)–C(2) = 1.341(7), Br–Pd–P(1) = 91.50(3), Br–Pd–P(2) = 95.55(3), C(1)–Pd–P(1) = 87.21(13), C(1)–Pd–P(2) = 85.75(13), Pd–C(1)–C(2) = 129.5(4), C(1)–C(2)–C(3) = 129.4(4).

Figure 1 shows ORTEP drawings of (E)-1a and (Z)-1a. Both complexes have similar structures with comparable distances of Pd–C (2.00 Å), Pd–P (2.31 Å), and Pd–Br (2.53 Å) bonds. A notable difference between the isomers is found for the orientation of styryl ligands. The (E)-styryl ligand in (E)-1a is oriented away from the palladium center, successfully evading the steric congestion within the molecule. On the other hand, the phenyl group of the (Z)-styryl ligand in (Z)-1a is situated over the palladium center. Although the interatomic distance of Pd···H(1) (2.494 Å) is in a range of agostic interaction, it seems likely to consider a repulsive interaction between them, because the C(1)–C(2)–C(3) angle (129.4(4)°) is significantly enlarged as compared with that of (E)-1a (123.4(2)°).
Figure 2. X-ray structures of (E)-2a and (Z)-2a. The thermal ellipsoids are drawn at the 30% probability levels. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows. (E)-2a: Pd–Br = 2.5669(10), Pd–P(2) = 2.281(2), Pd–C(1) = 2.135(8), Pd–C(2) = 2.063(7), C(1)–P(1) = 1.758(8), C(1)–C(2) = 1.444(10), C(2)–C(3) = 1.491(10), Br–Pd–P(2) = 98.32(6), C(1)–Pd–C(2) = 40.2(3), Pd–C(1)–C(2) = 67.2(4), C(1)–P–Br = 115.1(2), C(2)–Pd–P(2) = 106.4(2), C(1)–C(2)–C(3) = 122.0(7), P(1)–C(1)–P(2) = 122.2(6). (Z)-2a: Pd–Br = 2.6201(10), Pd–P(2) = 2.2872(17), Pd–C(1) = 2.106(5), Pd–C(2) = 2.088(5), C(1)–P(1) = 1.754(5), C(1)–C(2) = 1.438(7), C(2)–C(3) = 1.494(7), Br–Pd–P(2) = 92.78(4), C(1)–Pd–C(2) = 40.1(2), Pd–C(1)–C(2) = 69.3(3), C(1)–P–Br = 111.83(15), C(2)–P–P(2) = 115.24(16), C(1)–C(2)–C(3) = 124.8(4), P(1)–C(1)–P(2) = 129.6(4).

Figure 2 shows the X-ray structures of (E)-2a and (Z)-2a. The C(1)–C(2) distances (1.444(10), 1.438(7) Å) are comparable to each other. The Pd, C(1), C(2), P(2), and Br atoms are coplanar in both molecules as previously observed for related alkenylphosphonium complexes. The Pd–C(1) bonds (2.135(8), 2.106(5) Å) are apparently longer than the Pd–C(2) bonds (2.063(7), 2.088(5) Å), reflecting the higher trans-influence of PMePh₂ than Br.

A remarkable structural feature of (Z)-2a is the axial/axial/axial arrangement of three phenyl groups of PhCH=CHMePh and PMePh₂ ligands. Since they are situated at 1,3-diaxial positions with one another, a great deal of steric repulsion should take place.
between them. This situation makes a sharp contrast with \((E)-2a\), in which all substituents are accommodated with enough space. Actually, the P(1)–C(1)–C(2) angle of \((Z)-2a\) (129.6(4)°) is apparently wider than that of \((E)-2a\) (122.2(6)°).

**DFT Calculations.** Table 3 lists the relative energies of 2a to 1a, estimated by DFT calculations. The geometry optimization of \((E)-\) and \((Z)-\)isomers of the complexes was carried out using B3LYP in conjunction with the LANL2DZ basis set and effective core potential for Pd and 6-31G(d) basis set for other atoms, where diffuse function was added for Br atom. Solvent effects were incorporated by PCM single-point calculations on fully optimized geometries in vacuo. The optimized structures were in well accordance with the X-ray structures given in Figures 1 and 2.

The data in Table 3 clearly indicate that P–C reductive elimination of \((E)-\)isomer \([(E)-1a \rightarrow (E)-2a]\) is an exothermic process, whereas that of \((Z)-\)isomer \([(Z)-1a \rightarrow (Z)-2a]\) is endothermic (i.e., the reverse process is exothermic). It is also seen that 2a is more effectively stabilized than 1a in polar solvents, irrespective of the E/Z configurations of styryl group. These tendencies are consistent with the experimental observations described above.

### Table 3. Relative Energies of 2a to 1a (kcal mol\(^{-1}\))\(^a\)

<table>
<thead>
<tr>
<th>solvent</th>
<th>((E)-)isomers</th>
<th>((Z)-)isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>(in vacuo)</td>
<td>0.0</td>
<td>+4.3</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>−2.3</td>
<td>+2.3</td>
</tr>
<tr>
<td>THF</td>
<td>−4.2</td>
<td>+0.4</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>−4.6</td>
<td>+1.0</td>
</tr>
</tbody>
</table>

\(^a\)The values of \(E_{2a} – E_{1a}\), estimated by DFT calculations.
Figure 3. NBO charges on the core atoms of 1a and 2a. The values for (E)- and (Z)-isomers are given with roman and italic typefaces, respectively.

Figure 3 compares charge distribution in 1a and 2a, evaluated by NBO analysis. The values written in roman and italic letters correspond to the atomic charges for (E)- and (Z)-isomers, respectively. The $\eta^2$-styrylphosphonium palladium complexes (2) are commonly depicted as zwitter ionic species having positive and negative charges on the phosphorus and palladium atoms, respectively (see eqs 1 and 2). However, while the P(1) atom of 2a is charged positively, the Pd atom is not charged negatively in reality. The negative charge is distributed on the C(1), C(2) and Br atoms, and most remarkably increased on the C(1) atom as compared with 1a, showing the occurrence of strong $\pi$-back donation from the palladium center to the $\eta^2$-styrylphosphonium ligand in 2a.

Mechanism of P–C Reductive Elimination. As seen from Table 1 (runs 1, 2), the P–C reductive elimination of (E)-1a is strongly inhibited by added PMePh$_2$, showing a reaction process involving pre-dissociation of PMePh$_2$ ligand (path (a) in Scheme 1). The three-coordinate intermediate A undergoes P–C reductive elimination to form B, which combines with PMePh$_2$ to afford (E)-2a. On the other hand, as described below, kinetic data revealed that the other reaction process involving prior association of PMePh$_2$ is operative in the presence of added PMePh$_2$ (path (b)).
Scheme 1. Proposed Mechanisms for P–C Reductive Elimination of (E)-1a

Figure 4 shows the time-course of conversion of (E)-1a (50 mM) in CD$_2$Cl$_2$ at 40 °C, followed by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. In the absence of free PMePh$_2$ (run 1), the PMe signal of (E)-1a at $\delta$ 2.07 rapidly decreased ($t_{1/2}$ = ca. 5 min) to be replaced by the PMe signals of (E)-2a at $\delta$ 2.83 and 1.50. The reaction progress was effectively prevented by addition of a small amount of PMePh$_2$ (5 mM, 0.1 equiv/1a) to the system (run 2). In this case, however, the reaction dramatically accelerated from the middle stage, because the added PMePh$_2$ is consumed by trapping in the reductive elimination product as [Pd{η$^2$-(E)-PhCH=CHPMePh$_2$}(PMePh$_2$)$_2$]Br (E)-3a). Indeed, in the $^1$H NMR spectra, the PMe signal of (E)-1a was observed coalescent with that of PMePh$_2$ until ca. 20% conversion of (E)-1a, but thereafter changed to a sharp triplet, showing the absence of free PMePh$_2$ in the system.
Interestingly, the rate of P–C reductive elimination increased significantly with increasing amounts of added PMePh₂ (runs 3 and 4). Thus, the reaction performed with 50 mM of PMePh₂ (run 3) was clearly faster than the initial stage of run 2 (5 mM), and accelerated further with 200 mM of PMePh₂ (run 4). Although the concentration of free PMePh₂ gradually decreases with the formation of (E)-3a, the reactions obeyed a good first-order kinetics ($r > 0.999$) up to 19 (run 3) and 60% (run 4) conversion of (E)-1a. Table 4 lists the rate-constants ($k_{obsd}$) thus estimated. The plot of $1/k_{obsd}$ against $1/[\text{PMePh}_2]$ exhibited a good linear correlation ($r = 0.995$, Figure 5).

These kinetic observations are consistent with the reaction process of path (b) in Scheme 1. Since (E)-1a undergoes rapid ligand-exchange with free PMePh₂ in an NMR time-scale, it is likely to assume the occurrence of rapid equilibrium between (E)-1a and C. Intermediate C then undergoes the rate-determining formation of (E)-3a. In this case, the

**Figure 4.** The time-course of conversion of (E)-1a (50 mM) in CD₂Cl₂ at 40 °C in the absence or presence of added PMePh₂.
reaction rate can be expressed by eq 3, where \([\text{Pd-styryl}] = [(E)\text{-1a}] + [\text{C}],\) \(K = [\text{C}]/[(E)\text{-1a}][\text{PMePh}_2],\) and \(k\) stands for the rate-constant for the conversion of \(\text{C}\) to \((E)\text{-3a}:\)

\[
\frac{d[(E)\text{-3a}]}{dt} = -\frac{d[\text{Pd-styryl}]}{dt} = \frac{kK[\text{PMePh}_2]}{1 + K[\text{PMePh}_2]}[\text{Pd-styryl}]
\]

Consequently, the \(k_{\text{obsd}}\) values are correlated with the \([\text{PMePh}_2]\) values by the following equation:

\[
\frac{1}{k_{\text{obsd}}} = \frac{1}{kK[\text{PMePh}_2]} + \frac{1}{k}
\]

Applying the slope and intercept values of Figure 5 to eq 4 results in the following rate and equilibrium constants: \(k = 4.8 \times 10^{-4} \text{ s}^{-1}, K = 3.7 \text{ M}^{-1}.\)

**Table 4. Effects of Added PMePh\(_2\) on the First-order Rate Constants for P–C Reductive Elimination of \((E)\text{-1a}^a\)**

<table>
<thead>
<tr>
<th>[PMePh(_2)] (mM)</th>
<th>(10^4k_{\text{obsd}} \text{ s}^{-1})</th>
<th>data range (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.76(2)</td>
<td>19</td>
</tr>
<tr>
<td>64</td>
<td>0.87(1)</td>
<td>29</td>
</tr>
<tr>
<td>100</td>
<td>1.28(2)</td>
<td>38</td>
</tr>
<tr>
<td>200</td>
<td>2.14(1)</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^a\)\([(E)\text{-1a}]_0 = 50 \text{ mM. All reactions were run at 40 °C in CD}_2\text{Cl}_2.\)

\(^b\)The upper range of the conversion of \((E)\text{-1a},\) taken into the first-order plot.
Figure 5. Plot of $1/k_{\text{obsd}}$ against $1/\text{[PMePh}_2\text{]}$ for the kinetic data in Table 4. The straight line is based on least-squares calculation: $1/k_{\text{obsd}} = (5.7(4) \times 10^2 \text{ s M})/\text{[PMePh}_2\text{]} + (2.1(5) \times 10^3 \text{ s}).$

There are two possible structures for intermediate C. One is a five-coordinate species, whereas the other is a four-coordinate ionic complex [Pd{CH=CHPh-($E$)}(PMePh$_2$)$_3$]$^+$Br$^-$ (($E$)-4a), generated by ligand displacement of Br in ($E$)-1a with PMePh$_2$. The P–C reductive elimination from the latter type intermediate has been postulated for catalytic conversion of alkenyl triflates and PPh$_3$ to alkenylphosphonium triflates.$^{5c,d}$ The author therefore prepared [Pd{CH=CHPh-($E$)}(PMePh$_2$)$_3$]$^+$OTf$^-$ (($E$)-5a) as a model of ($E$)-4a, and examined its reactivity toward P–C reductive elimination (eq 5).
Treatment of \((E)-1a\) (50 mM) with AgOTf (1 equiv) in CD$_2$Cl$_2$ in the presence of PMePh$_2$ (1 equiv) at –30 °C for 1 h formed \((E)-5a\) in 96% selectivity. The resulting \((E)-5a\) was highly reactive toward P–C reductive elimination; the reaction was completed within a few minutes at 40 °C to give [Pd\{η$^2$-(E)-PhCH=CHPMePh$_2$\}(PMePh$_2$)$_2$]OTf ((E)-6a) in 95% selectivity. No notable change in the reaction rate was observed in the presence of excess PMePh$_2$ (4 equiv). Since the observed reactivity of \((E)-5a\) \((k > 5 \times 10^{-3} \text{ s}^{-1} \text{ at } 40 \text{ °C})\) is at least 10 times higher than that of \(C\) \((k = 4.8 \times 10^{-4} \text{ s}^{-1})\), it is convincing that \(C\) is not the ionic species like \((E)-5a\), but either a five-coordinate species or a tight ion pair of [Pd\{CH=CHPh-(E)\}(PMePh$_2$)$_3$]$^+$ and Br$^-$. Complex \(C\) is then converted to \((E)-3a\) by either a stepwise mechanism involving a metallophosphorane intermediate [Pd\{P(Ch=CHPh)MePh$_2$\}Br(PMePh$_2$)$_2$]$_{13}$ or a concerted mechanism with concurrent formation of the P–CH=CH and Pd–(η$^2$-CH=CH) bonds.

**Conclusions**

It has been evidenced that P–C reductive elimination of trans-[Pd\{(CH=CHPh)-Br(PMePh$_2$)$_2$\} \((1a)\) is essentially a reverse process with P–C oxidative addition of styrylphosphonium complex [Pd\{η$^2$-PhCH=CHPMePh$_2$\}Br(PMePh$_2$)] \((2a)\). The interconversion between \(1a\) and \(2a\) is markedly dependent on E/Z configurations of styryl group and solvent polarity. The \((E)\)-isomer of \(1a\) undergoes P–C reductive elimination easily in polar CD$_2$Cl$_2$ to afford \((E)-2a\) in high selectivity, whereas P–C oxidative addition of \((Z)-2a\) giving \((Z)-1a\) takes place favorably in non-polar C$_6$D$_6$. These tendencies have been rationalized by X-ray structural analysis and DFT calculations for \(1a\) and \(2a\). Complex \(2a\) bearing styrylphosphonium ligand is a significantly charged molecule, compared with \(1a\), to cause a strong solvent effect. Moreover, complex \((Z)-2a\) is sterically unstable due to the occurrence of 1,3-diaxial interactions of phenyl groups within the molecule, and thereby converted to \((Z)-1a\) by P–C oxidative addition.
The reductive elimination from [PdR(R’)L₂] type complexes has been known to proceed via any of three reaction processes: (a) dissociative path via a three-coordinate intermediate, (b) direct path, and (c) associative path with pre-coordination of an external L to give a [PdR(R’)L₃] intermediate.¹ᵃ The reaction processes vary with hydrocarbyl ligands, and alkenyl complexes generally follow the direct path (b).¹⁴ On the other hand, the present P–C reductive elimination from (E)-1a has been found to proceed via either dissociative path (a) or associative path (c), depending on the amount of free PMePh₂ in the system. In the absence of free PMePh₂, the reaction invokes pre-dissociation of one of the PMePh₂ ligands, giving a three-coordinate [Pd(CH=CHPh)Br(PMePh₂)] intermediate, which undergoes P–C reductive elimination. This process is effectively suppressed by addition of PMePh₂ to the system, and an alternative process involving prior association of (E)-1a with PMePh₂ takes place. Comparison of the kinetic data with that of [Pd{CH=CHPh-(E)}(PMePh₂)₃]⁺OTF⁻ ((E)-5a) has suggested the intermediacy of a five-coordinate species or a tight ion pair of [Pd{CH=CHPh-(E)}(PMePh₂)₃]⁺ and Br⁻, rather than the four-coordinate ionic species like (E)-5a.

**Experimental Section**

**General Considerations.** All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Nitrogen and argon gases were dried by passing through P₂O₅ (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (¹H NMR 400.13 MHz, ¹³C NMR 100.62 MHz, and ³¹P NMR 161.97 MHz). Chemical shifts are reported in δ (ppm), referenced to the ¹H (residual protons) and ¹³C signals of deuterated solvents or to the ³¹P signal of an external 85% H₃PO₄ standard. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. CD₂Cl₂, THF-d₈, and C₆D₆ were dried over CaH₂, Na/Ph₂CO, and LiAlH₄, respectively, distilled, and stored over activated MS4A. The compounds trans-[Pd{CH=CHPh-(E)}]-
P–C Reductive Elimination

Br(PMePh\textsubscript{2})\textsubscript{2}] ((E)-1a),\textsuperscript{11} trans-[Pd\{CH=CH(\textit{Z})Br(PMePh\textsubscript{2})\textsubscript{2}] ((Z)-1a),\textsuperscript{14a} [Pd\{\textit{η}\textsuperscript{2}-(E)-Ph-CH=CHPMePh\textsubscript{2}\}Br(PMePh\textsubscript{2})] ((E)-2a),\textsuperscript{11} [Pd(\textit{η}\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})(\textit{η}\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3})],\textsuperscript{15} (E)-styryl bromide,\textsuperscript{16} (Z)-P(\textit{CH}=\textit{CH}Ph)Ph\textsubscript{2},\textsuperscript{17} and [Pd(db\textsubscript{a})\textsubscript{2}]\textsuperscript{18} were prepared according to literatures. Other chemicals were purchased and used as received.

**Synthesis of trans-[Pd\{CH=CH(\textit{E})\}Br(PPh\textsubscript{3})\textsubscript{2}] ((E)-1b).** To a heterogeneous solution of [Pd(\textit{η}\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})(\textit{η}\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3})] (106 mg, 0.500 mmol) and PPh\textsubscript{3} (275 mg, 1.05 mmol) in toluene (10 mL) was added (E)-styryl bromide (1.83 g, 10.0 mmol) at 0 °C. The mixture was stirred at room temperature until being homogeneous, and then was allowed to stand at the same temperature, causing precipitation of pale yellow crystals of (E)-1b, which was collected by filtration, washed successively with Et\textsubscript{2}O, and dried under vacuum (385 mg, 95% yield). The NMR data was identical to those reported.\textsuperscript{12} \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 7.70–7.63 \) and \( \delta 7.43–7.30 \) (m, 30H in total), \( \delta 6.98–6.87 \) (m, 3H), \( \delta 6.40 \) (dt, \( 3J_{HH} = 15.7 \) Hz, \( 3J_{HP} = 9.7 \) Hz, 1H), \( \delta 6.27 \) (d, \( 3J_{HH} = 6.8 \) Hz, 2H), \( \delta 5.42 \) (dt, \( 3J_{HH} = 15.8 \) Hz, \( 4J_{HP} = 2.5 \) Hz, 1H). \( 31\text{P}\{\text{\textsuperscript{1}H}\} \) NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 24.5 \) (s).

**Synthesis of trans-[Pd\{CH=CH(\textit{E})\}Br(PMe\textsubscript{3})\textsubscript{2}] ((E)-1c).** To a homogeneous solution of [(\textit{η}\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})(\textit{η}\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3})Pd] (106 mg, 0.500 mmol) in toluene (2.0 mL) was added PMe\textsubscript{3} (78.9 mg, 1.05 mmol) at 0 °C. The mixture was stirred for 10 min, and (E)-styryl bromide (366 mg, 2.00 mmol) was added. The solution was stirred at room temperature for 4 h. Hexane (5 mL) was added with stirring at 0 °C. A white precipitate formed in the system was collected by filtration, washed successively with hexane (2 \times 2 mL) and Et\textsubscript{2}O (2 \times 2 mL), and dried under vacuum. The crude product was dissolved in a minimum amount of CH\textsubscript{2}Cl\textsubscript{2} (ca. 1 mL) at room temperature, layered with Et\textsubscript{2}O (ca. 5 mL), and allowed to stand at the same temperature to afford pale yellow crystals of the title compound (165 mg, 74% yield). Mp: 118–120 °C (dec). \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 7.33–7.21 \) and \( \delta 7.12–7.07 \) (m, 6H in total), \( \delta 6.43 \) (d, \( 3J_{HH} = 16.5 \) Hz, 1H), 1.38 (virtual triplet, \( J = 3.5 \) Hz, 18H). \( 13\text{C}\{\text{\textsuperscript{1}H}\} \) NMR (CD\textsubscript{2}Cl\textsubscript{2}): \( \delta 145.6 \) (t, \( 3J_{PC} = 9 \) Hz), 140.4 (s), 134.3 (t, \( 4J_{PC} = 6 \) Hz), 129.0 (s), 125.9 (s), 125.2 (s), 14.6 (t,
\( J_{PC} = 15 \text{ Hz} \). \( ^{31}P\{^1H\} \text{ NMR (CD}_2\text{Cl}_2\): } \delta -17.9 \text{ (s). Anal. Caled for C}_{14}H_{25}\text{BrP}_2\text{Pd: C, 38.08; H, 5.71. Found: C, 37.96; H, 5.68.}

**Synthesis of [Pd\{Z\}-PhCH=CHPMePh\textsubscript{2}\}Br\textsubscript{2}(PMePh\textsubscript{2})\] ((Z)-2a).** (a) Synthesis of (Z)-[PhCH=CHPMePh\textsubscript{2}\}Br\textsubscript{2}. A mixture of (Z)-P(CH=CHPh)Ph\textsubscript{2} (1.22 g, 4.25 mmol) and 2 M solution of MeBr in THF (22 mL, 44 mmol) was stirred at room temperature. After 48 h, a white precipitate generated from the solution was collected by filtration, washed successively with Et\textsubscript{2}O, and dried under vacuum. Recrystallization of the crude product from a mixture of acetone and Et\textsubscript{2}O at –20 °C gave pale yellow crystals of the title compound (1.33 g, 82% yield). Mp: 130 °C. \(^1H\text{ NMR (CDCl}_3\): } \delta 8.30 (dd, \(^2J_{HP} = 45.4 \text{ Hz}, \(^3J_{HH} = 13.2 \text{ Hz}, 1H), 7.86–7.78, 7.73–7.67 \text{ and } 7.63–7.57 \text{ (m, 10H in total)}, 7.22 (t, \(^3J_{HH} = 7.4 \text{ Hz}, 1H), 7.13–7.05 \text{ (m, 3H)}, 7.01 (d, \(^3J_{HH} = 7.6 \text{ Hz}, 2H), 2.74 (d, \(^3J_{HP} = 13.5 \text{ Hz}, 3H). \(^13C\{^1H\} \text{ NMR (CDCl}_3\): } \delta 158.0 (d, \(^4J_{PC} = 1 \text{ Hz}), 134.6 (d, \(^2J_{PC} = 3 \text{ Hz}), 133.5 (d, \(^3J_{PC} = 8 \text{ Hz}), 132.6 (d, \(^3J_{PC} = 11 \text{ Hz}), 130.4 (s), 130.3 (d, \(^2J_{PC} = 13 \text{ Hz}), 128.5 (s), 128.4 (d, \(^4J_{PC} = 2 \text{ Hz}), 120.2 (d, \(^1J_{PC} = 89 \text{ Hz}), 110.0 (d, \(^1J_{PC} = 82 \text{ Hz}), 12.2 (d, \(^1J_{PC} = 58 \text{ Hz}). \(^{31}P\{^1H\} \text{ NMR (CDCl}_3\): } \delta 12.9 \text{ (s). Anal. Caled for C}_{21}H_{20}\text{BrP: C, 65.81; H, 5.26. Found: C, 65.67; H, 5.36.}

(b) Synthesis of (Z)-2a. The complex [Pd\{dba\}_2\] (288 mg, 0.500 mmol) and (Z)-[PhCH=CHPMePh\textsubscript{2}\}Br\textsubscript{2} (192 mg, 0.500 mmol) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (10 mL), and PMePh\textsubscript{2} (100 mg, 0.500 mmol) was added at room temperature. The mixture was stirred for 1 h, and filtered through a Celite pad, and the filtrate was concentrated to dryness under reduced pressure. The residue was extracted three-times with a mixed solvent of THF (2 mL) and Et\textsubscript{2}O, and the combined extract was concentrated to dryness to give a pale yellow solid of (Z)-2a. This product was purified three-times by reprecipitation from CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O (1/15 mL) at –78 °C, and then by recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O at –20 °C (162 mg, 47% yield). Mp: 117–119 °C (dec), \(^1H\text{ NMR (CD}_2\text{Cl}_2\): } \delta 7.87–7.80, 7.71–7.64, 7.64–7.45, \text{ and } 7.31–7.20 \text{ (m, 20H in total)}, 6.81 (d, \(^3J_{HH} = 7.0 \text{ Hz}, 2H), 6.76 (t, \(^3J_{HH} = 7.3 \text{ Hz}, 1H), 6.57 (t, \(^3J_{HH} = 7.7 \text{ Hz}, 2H), 4.51 (ddd, \(^2J_{HP} = 27.3 \text{ Hz}, \(^3J_{HH} = 10.7 \text{ Hz}, \(^3J_{HP} = 5.3 \text{ Hz}, 1H), 2.87 (ddd, \(^3J_{HP} = 11.9 \text{ Hz}, \(^3J_{HH} = 10.7 \text{ Hz}, \(^2J_{HP} = 8.1 \text{ Hz}, 1H), 2.58 (d, \(^3J_{HP} = 13.6 \text{ Hz}, 3H), 1.71 (d, \(^2J_{HP} = 6.1 \text{ Hz,
P–C Reductive Elimination and Oxidative Addition. A typical procedure is as follows. ((E)-1a (20.7 mg, 0.030 mmol) and 1,3,5-trimethoxybenzene (2.5 mg, 0.015 mmol; internal standard) were placed in an NMR sample tube, and dissolved in CD$_2$Cl$_2$ (total 0.6 mL) at room temperature under an argon atmosphere. The sample tube was placed in an NMR sample probe controlled to 40.0 ± 0.1 °C. The reaction was examined at intervals by $^1$H NMR spectroscopy using the following marker signals: ((E)-1a ($\delta$ 2.07, PMe), (E)-2a ($\delta$ 2.83, PMe), (E)-3a (d 1.18, PMe), trans-[PdBr$_2$(PMePh$_2$)$_2$] ($\delta$ 2.24, PMe).

The complex [Pd{η$^2$-(E)-PhCH=CHPMePh$_2$}(PMePh$_2$)$_2$]Br (((E)-3a) was independently prepared from (E)-2a and PMePh$_2$ (1 equiv) in CD$_2$Cl$_2$, and characterized by NMR spectroscopy. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.81–7.21, 7.20–7.05, 6.73–6.67, and 6.67–6.55 (m, 35H in total), 3.74–3.58 (m, 2H), 1.98 (d, $^2$J$_{HP}$ = 13.1 Hz, 3H), 1.59 (d, $^2$J$_{HP}$ = 4.9 Hz, 3H), 1.12 (d, $^2$J$_{HP}$ = 6.1 Hz, 3H). $^{31}$P$^{1}$H NMR (CD$_2$Cl$_2$): $\delta$ 21.4 (br), 4.5 (br), 4.2 (br). The formation of (E)-3a took place instantly at room temperature, as already documented for (E)-3b.

Synthesis and P–C Reductive Elimination of [Pd{CH=CHPh-(E)}(PMePh$_2$)$_3$]OTf ((E)-5a). Complex (E)-1a (27.6 mg, 0.0400 mmol), PMePh$_2$ (8.0 mg, 0.040 mmol), and 1,3,5-trimethoxybenzene (3.4 mg, 0.020 mmol; internal standard) were dissolved in CD$_2$Cl$_2$ (0.75 mL), and AgOTf (10.3 mg, 0.400 mmol) was added at –30 °C. The solution was stirred at this temperature for 1 h to precipitate an off-white powder of AgBr. The orange supernatant was transferred by cannulation to an NMR sample tube, and analyzed by $^1$H NMR.
spectroscopy at −30 °C, showing the formation of (E)-5a (96%) and a small amount of [Pd{η²-(E)-PhCH=CHPMePh₂}(PMePh₂)₂]OTf ((E)-6a) (3%). At 40 °C, (E)-5a was converted to (E)-6a within 4 min in 95% selectivity. Since (E)-5a was thermally too unstable to be isolated, its characterization was carried out by NMR spectroscopy.

(E)-5a. ¹H NMR (CD₂Cl₂, −30 °C): δ 7.46–7.15 and 7.02–6.92 (m, 33H in total), 6.29 (dd, ³J_HH = 7.3 Hz, 2H), 6.14 (tdd, ³J_HH = 20.6 Hz, ³J_HH = 16.6 Hz, ³J_HH = 10.5 Hz, 1H), 5.72 (dd, ³J_HH = 16.6 Hz, ⁴J_HH = 10.2 Hz, 1H), 1.66 (virtual triplet, ³J_HP = 7.2 Hz, 3H). ¹³P{¹H} NMR (CD₂Cl₂, −30 °C): δ 7.9 (d, ²J_PP = 35 Hz), −0.53 (t, ²J_PP = 35 Hz).

(E)-6a. ¹H NMR (CD₂Cl₂): δ 7.82–7.76, 7.70–7.56, 7.52–7.23, 7.16–7.10, 6.72–6.66, and 6.66–6.56 (m, 35H in total), 3.72–3.51 (m, 2H), 1.85 (d, ²J_HP = 13.1 Hz, 3H), 1.57 (d, ²J_HP = 5.3 Hz, 3H), 1.12 (d, ²J_HP = 6.1 Hz, 3H). ¹³C{¹H} NMR (CD₂Cl₂): δ 142.1 (dd, ³J_PC = 12 Hz, ³J_PC = 7 Hz), 138.5 (dd, ¹J_PC = 29 Hz, ³J_PC = 3 Hz), 137.5 (dd, ¹J_PC = 31 Hz, ³J_PC = 3 Hz), 136.8 (dd, ¹J_PC = 30 Hz, ³J_PC = 1 Hz), 134.5 (d, ⁴J_PC = 3 Hz), 134.4 (d, ⁴J_PC = 3 Hz), 134.4 (d, ²J_PC = 14 Hz), 132.3 (d, ²J_PC = 14 Hz), 131.7 (d, ²J_PC = 14 Hz), 131.2 (d, ²J_PC = 13 Hz), 130.7 (d, ²J_PC = 1 Hz), 130.3 (d, ²J_PC = 12 Hz), 130.2 (s), 130.1 (d, ²J_PC = 12 Hz), 129.6 (d, ⁴J_PC = 1 Hz), 129.4 (d, ³J_PC = 9 Hz), 129.4 (d, ³J_PC = 9 Hz), 129.2 (m), 128.8 (d, ³J_PC = 9 Hz), 128.7 (d, ³J_PC = 9 Hz), 126.2 (m), 125.2 (m), 124.6 (dd, ¹J_PC = 89 Hz, ³J_PC = 2 Hz), 124.4 (dd, ¹J_PC = 83 Hz, ³J_PC = 5 Hz), 121.6 (q, ¹J_PC = 321 Hz), 65.7 (dd, ²J_PC = 31 Hz, ²J_PC = 5 Hz), 34.0 (dd, ¹J_PC = 79 Hz, ²J_PC = 32 Hz, ²J_PC = 7 Hz), 15.1 (d, ¹J_PC = 19 Hz), 13.0 (d, ¹J_PC = 20 Hz), 11.6 (d, ¹J_PC = 64 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ 21.3 (d, ²J_PP = 12 Hz), 4.4 (s), 4.1 (d, ²J_PP = 12 Hz).

X-ray Structural Analysis. Single crystals of (E)-1a, (Z)-1a, (E)-2a, and (Z)-2a were grown by slow diffusion of Et₂O into CH₂Cl₂ solutions at −20 °C ((E)-1a, (E)-2a, (Z)-2a) and −30 °C ((Z)-1a), respectively. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The intensity data were collected at 173 K and corrected for Lorentz and polarization effects and for
absorption. The structures were solved by heavy atom Patterson methods (PATTY), expanded using Fourier techniques (DIRDIF99), and refined on \( F^2 \) for all reflections (SHELXL97). All non-hydrogen atoms were refined anisotropically. The H(1) atom of (Z)-1a was located from a differential Fourier map and refined isotropically. The other hydrogen atoms were placed using AFIX instructions. Crystal data and details of data collection and refinement are summarized in Table 5 and 6.

**Computational Details.** All calculations were performed using B3LYP level of density functional theory. The Pd atom was described using LANL2DZ basis set including a double-\( \zeta \) basis set with the Hay and Wadt effective core potential (ECP). The 6-31G(d) basis set was used for other atoms. Diffuse function was added for Br atom. Frequency calculations were carried out to identify all the stationary states as minima (zero imaginary frequencies). All calculations in this study have been performed without any symmetry constraints using the Gaussian 03. The solvent effect was taken into account through single-point calculations at each optimized geometry in vacuo using the polarized continuum model (PCM) at 298.15 K. The partial atomic charges were calculated on the basis of natural bond orbital (NBO) analyses.
Table 5. Crystal Data and Details of the Structure Determination for 1a

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Table 6. Crystal Data and Details of the Structure Determination for 2a

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</tr>
<tr>
<td>β (deg)</td>
<td>109.107(3)</td>
<td>84.226(13)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>80.528(12)</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>2999.4(10)</td>
<td>1480.9(9)</td>
</tr>
<tr>
<td>(d_{\text{calc}}) (cm\textsuperscript{-3})</td>
<td>1.523</td>
<td>1.547</td>
</tr>
<tr>
<td>space group</td>
<td>Cc (#9)</td>
<td>P(–1) (#2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(\mu) (mm\textsuperscript{-1})</td>
<td>2.079</td>
<td>2.106</td>
</tr>
<tr>
<td>transmission factors</td>
<td>0.5936–0.7060</td>
<td>0.6781–0.6781</td>
</tr>
<tr>
<td>absorption correction</td>
<td>numerical</td>
<td>empirical</td>
</tr>
<tr>
<td>θ range (deg)</td>
<td>3.23–27.48</td>
<td>3.08–27.48</td>
</tr>
<tr>
<td>no. of reflns collected</td>
<td>12140</td>
<td>12141</td>
</tr>
<tr>
<td>no. of unique reflns</td>
<td>5855 ((R_{\text{int}} = 0.0267))</td>
<td>6521 ((R_{\text{int}} = 0.0541))</td>
</tr>
<tr>
<td>no. of reflns with (I &gt; 2σ(I))</td>
<td>4546</td>
<td>4103</td>
</tr>
<tr>
<td>no. of variables (restraints)</td>
<td>338 (2)</td>
<td>345 (0)</td>
</tr>
<tr>
<td>GOF on (F^2)</td>
<td>1.048</td>
<td>1.059</td>
</tr>
<tr>
<td>final (R) indices ((I &gt; 2σ(I)))</td>
<td>(R_1 = 0.0496, wR_2 = 0.1335)</td>
<td>(R_1 = 0.0545, wR_2 = 0.0898)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.0586, wR_2 = 0.1374)</td>
<td>(R_1 = 0.1015, wR_2 = 0.1121)</td>
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<tr>
<td>max and min peak (e Å\textsuperscript{-3})</td>
<td>0.984, –0.900</td>
<td>1.099, –0.865</td>
</tr>
</tbody>
</table>
References and notes


(10) The P–C reductive elimination of styryl complex has been reported for trans-[Pd{CH=CHPh-(E)}Br(PPh3)2] (1b)5a


(12) The PPh3 analogue [Pd{η2-(E)-PhCH=CHPPh3}(PPh3)2]Br ((E)-3b) has been reported.5a


P–C Reductive Elimination


(20) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.


Chapter 5

Stereocontrolled Synthesis and Photo-induced Insolubilization of All-trans Poly(arylenevinylene)s

Abstract

To achieve highly selective synthesis of all-trans poly[(p-phenylenevinylene)-alt-(2,5-dioctyloxy-1,4-phenylenevinylene)]s (3) by Suzuki–Miyaura-type polycondensation of (E,E)-1,4-bis(2-bromoethenyl)benzene (1) and 2,5-dioctyloxybenzene-1,4-diboronic acid (2), appropriate catalytic conditions have been investigated using (E)-styryl bromide (4) and 2,5-dioctyloxybenzeneboronic acid (5) as model compounds of 1 and 2, respectively. The reaction of 4 and 5 in toluene in the presence of [Pd(PPh₃)₄] catalyst and aqueous K₂CO₃ base affords considerable amounts of homo-coupling products (i.e., 1,4-diphenylbutadiene (13%) and 2,2’-5,5’-tetraoctyloxybiphenyl (22%)), together with (E)-2,5-dioctyloxystilbene (6) as the cross-coupling product (30%). The amounts of homo-coupling products are reduced effectively by using aqueous NaOH as a base and Bu₄NBr as a phase-transfer catalyst. Moreover, the use of [Pd(PBu’₃)₂] instead of [Pd(PPh₃)₄] leads to almost perfect selectivity of 6 under mild conditions. Hence the desired all-trans 3 has been successfully prepared without notable defects in the polymer chain. Photochemical properties of all-trans 3 in thin films are described.
Introduction

Poly(phenylenevinylene)s (PPVs) and their homologues (i.e., poly(arylenevinylene)s: PAVs) are among the π-conjugated polymers that have wide application in optoelectronic and biological devices such as light-emitting diodes (LEDs),\textsuperscript{1,2} photovoltaic devices,\textsuperscript{3} plastic lasers,\textsuperscript{4} and field-effect transistors (FETs).\textsuperscript{5} They have been synthesized by a variety of methods, including thermolysis of sulfonium polymer precursors (Wessling),\textsuperscript{6} dehydrohalogenative polycondensation of bis(halomethyl)benzenes (Gilch),\textsuperscript{7} Wittig–Horner-type polycondensation of diphosphonates with phthaldehydes,\textsuperscript{8} ring-opening metathesis polymerization (ROMP),\textsuperscript{9} acyclic diene metathesis (ADMET),\textsuperscript{10} and palladium-catalyzed polycondensations using cross-coupling reactions (Mizoroki–Heck,\textsuperscript{11} Migita–Kosugi–Stille,\textsuperscript{12} and Hiyama\textsuperscript{13,14}), and most of them afford all-trans or trans-rich PAVs having trans-vinylene linkages. On the other hand, our research group has recently reported that all-cis PAVs having the vinylene linkages entirely controlled to cis geometry are successfully prepared by Suzuki–Miyaura-type polycondensation of (Z,Z)-bis(2-bromoethenyl)arenes with 2,5-dioctyloxybenzene-1,4-diboronic acid.\textsuperscript{15} It has also been found that all-cis PAVs thus prepared exhibit unique photochemical properties; namely, the polymers undergo one-way photoisomerization to all-trans isomers in thin films, and the resulting films become much less soluble than before photo-irradiation.\textsuperscript{15a} This phenomenon (i.e., photo-induced insolubilization) should be useful for fabricating multilayered devices of π-conjugated polymers by solution processes.\textsuperscript{16}

In Chapter 1, the author investigated this phenomenon using all-cis poly(p-phenylenevinylene)s (PpPVs) in detail, and found that the photo-induced insolubilization is significantly facilitated when the polymers bear a 2-bromoethenyl group at the chain end, which is derived from (Z,Z)-bis(2-bromoethenyl)benzene as a substrate of Suzuki–Miyaura-type polycondensation. Thus, although the insolubilization in thin films have so far been observed only for all-cis PpPVs, and all-trans PpPV independently prepared by Hiyama-type polycondensation does not show this phenomenon,\textsuperscript{17} there is a possibility that all-trans PpPVs with the same
terminal structures are insolubilized by UV-irradiation as well. Accordingly, the author prepared all-trans PpPVs (3) via Suzuki–Miyaura-type polycondensation of (E,E)-1,4-bis(2-bromoethenyl)benzene (1) with 2,5-dioctyloxybenzene-1,4-diboronic acid (2) (eq 1), and examined their photochemical properties in thin films.

\[ \text{(E,E)-1} + \text{(XO)}_2\text{B} \rightarrow \text{OC}_8\text{H}_{17} \]

\[ \text{Pd cat.} \]

\[ \text{base, additive} \]

\[ \rightarrow \text{OC}_8\text{H}_{17} \]

\[ \text{all-trans 3} \]
Results and Discussion

Examination of Catalytic Conditions. As demonstrated in Chapter 3, unlike the reaction of (Z)-styryl bromide, the Suzuki–Miyaura cross-coupling of (E)-styryl bromide with PhB(OH)₂ is very prone to compete with homo-coupling giving 1,4-diphenylbutadiene and biphenyl. Because the homo-coupling reaction causes defects in polymer chains upon polycondensation, a highly selective system for cross-coupling was pursued by using (E)-styryl bromide (4) and 2,5-dioctyloxybenzeneboronic acid (5) as the model compounds of (E,E)-1 and 2 in eq 1, respectively (eq 2). Table 1 summarizes the results. The reaction of (E)-4 with 5 in toluene at 80 °C in the presence of [Pd(PPh₃)₄] (1.5 mol%) and aqueous K₂CO₃ (3 equiv) afforded four kinds of products; i.e., cross-coupling product 6 (30%), homo-coupling products 7 (13%) and 8 (22%), and a trace amount of 1,4-dioctyloxybenzene (9), formed by hydrolysis of 5 (entry 1).

\[
\text{Ph} \overset{\text{Br}}{\text{–}} \text{Ph} \quad \overset{\text{Pd cat. (1.5 mol%)}}{\text{+}} \quad \text{Ar – B(OH)₂} \quad \overset{\text{base (3 equiv)}}{\text{→}} \quad \text{toluene, 80 °C} \\
\]

(2)

It is accepted that the Suzuki–Miyaura reaction proceeds via three elementary processes. As for the reaction of eq 2, the first step is the oxidative addition of (E)-4 to a palladium(0) species [Pd(PR₃)ₙ] (process (i)). The resulting [Pd(CH=CHPh)(Br)(PR₃)₂] undergoes transmetalation with 5 with the aid of a base to give [Pd(CH=CHPh)(Ar)(PR₃)₂] (process (ii)), which reductively eliminates 6 (process (iii)). The homo-coupling process competes with the transmetalation process (ii). In Chapter 3, the author confirmed that the
homo-coupling product 7 is afforded by the reaction of [Pd(CH=CHPh)Br(PR₃)₂] with (E)-4. Moreover, [PdBr₂(PR₃)₂] generated concurrently with 7 in the system reacts with 5 in the presence of a base to give 8. Interestingly, the formation of 7 is catalyzed by [Pd(η²-PhCH=CHRPR₃)Br(PR₃)], which is provided from [Pd(CH=CHPh)Br(PR₃)₂] by P–C reductive elimination of the styryl and phosphine ligands. Taking these mechanistic findings into consideration, the author examined the catalytic conditions to facilitate the transmetalation process, compared with the homo-coupling process.

First, the reaction was examined using a variety of bases (entries 1–8). It has been known that the association with a base is essential for the areneboronic acid to gain the nucleophilicity required for the transmetalation.¹⁸ Actually, aqueous NaOH as a strong base notably enhanced the reactivity and selectivity for cross-coupling (entry 4), while aqueous KOH was not so effective (entry 5). The other bases including metal carbonates (entries 1 and 2), phosphate (entry 3), and fluorides (entries 6 and 7) were much less effective, and silver oxide mainly caused hydrolysis of 5 to give 9 (entry 8). The reactivity and selectivity of the reactions using aqueous NaOH and KOH bases were greatly improved by addition of Bu₄NBr or (Octyl)₃MeNCl to the system (entries 9–11). It is reasonable that the ammonium salts, serving as a phase-transfer catalyst in a two-phase system consisting of toluene and water, enhance the efficiency of a base, thereby facilitating the transmetalation process. The combination of aqueous NaOH and Bu₄NBr was particularly effective, giving a quantitative yield of 6 (entry 9).

Next, basic and bulky tertiary phosphine ligands were examined as another approach to a highly selective system for the cross-coupling of (E)-styryl bromide (4) and areneboronic acid (5). As described above, the homo-coupling proceeds via a unique reaction process induced by P–C reductive elimination of [Pd(CH=CHPh)Br(PR₃)₂] intermediate. As shown in Chapter 4, the P–C reductive elimination is significantly decelerated when the tertiary phosphine ligands are highly basic. The author also anticipated that a bulky ligand provides a highly coordinatively unsaturated species, suitable for transmetalation as a ligand displacement process. As seen from entries 13–16 in Table 1, PCy₃ was insufficient (entry
but more bulky PbBu\textsubscript{3} resulted in almost quantitative yields of 6, even in the absence of Bu\textsubscript{4}NBr (entries 13, 14 and 16). The reaction smoothly proceeded even at room temperature (entry 15).

Table 1. Suzuki–Miyaura Cross-Coupling of (E)-4 and 5\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>Pd cat.</th>
<th>base\textsuperscript{b}</th>
<th>additive</th>
<th>time (h)</th>
<th>yield (%)\textsuperscript{c}</th>
<th>6\textsuperscript{d}</th>
<th>7\textsuperscript{e}</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq K\textsubscript{2}CO\textsubscript{3} none</td>
<td>2</td>
<td>30 (97/3)</td>
<td>13 (29/71)</td>
<td>22</td>
<td>&gt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq Cs\textsubscript{2}CO\textsubscript{3} none</td>
<td>2</td>
<td>25 (99/1)</td>
<td>11 (18/82)</td>
<td>18</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq K\textsubscript{3}PO\textsubscript{4} none</td>
<td>2</td>
<td>31 (96/4)</td>
<td>11 (22/78)</td>
<td>20</td>
<td>&gt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq NaOH none</td>
<td>2</td>
<td>95 (&gt;99/1)</td>
<td>4 (42/58)</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq KOH none</td>
<td>2</td>
<td>72 (98/2)</td>
<td>27 (18/82)</td>
<td>20</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq KF none</td>
<td>2</td>
<td>20 (98/2)</td>
<td>9 (28/72)</td>
<td>15</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq CsF none</td>
<td>2</td>
<td>21 (99/1)</td>
<td>10 (22/78)</td>
<td>16</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq Ag\textsubscript{2}O none</td>
<td>2</td>
<td>22 (98/2)</td>
<td>6 (77/23)</td>
<td>4</td>
<td>74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq NaOH Bu\textsubscript{4}NBr</td>
<td>1</td>
<td>99 (&gt;99/1)\textsuperscript{g}</td>
<td>0</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq KOH Bu\textsubscript{4}NBr</td>
<td>1</td>
<td>97 (&gt;99/1)</td>
<td>0</td>
<td>1</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>[Pd(PPh\textsubscript{3})\textsubscript{4}] aq NaOH (Octyl)\textsubscript{3}MeNCl</td>
<td>1</td>
<td>97 (&gt;99/1)</td>
<td>0</td>
<td>3</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>[Pd(PCy\textsubscript{3})\textsubscript{2}] aq KOH none</td>
<td>3</td>
<td>83 (99/1)</td>
<td>10 (16/84)</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>[Pd(PBu\textsubscript{3})\textsubscript{2}] aq NaOH none</td>
<td>1</td>
<td>96 (&gt;99/1)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>[Pd(PBu\textsubscript{3})\textsubscript{2}] aq KOH none</td>
<td>1</td>
<td>97 (&gt;99/1)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15\textsuperscript{f}</td>
<td>[Pd(PBu\textsubscript{3})\textsubscript{2}] aq NaOH none</td>
<td>1</td>
<td>98 (&gt;99/1)</td>
<td>0</td>
<td>&lt;1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>[Pd(PBu\textsubscript{3})\textsubscript{2}] aq NaOH Bu\textsubscript{4}NBr</td>
<td>1</td>
<td>98 (&gt;99/1)\textsuperscript{h}</td>
<td>0</td>
<td>&lt;1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reactions were run in a 0.20 mmol scale in toluene (1 mL) at 80 °C unless otherwise noted.
\textsuperscript{b}All bases were employed as 3 M aqueous solutions. \textsuperscript{c}Determined by \textsuperscript{1}H NMR spectroscopy using hexamethylbenzene as an internal standard. \textsuperscript{d}The (E)/(Z) ratios of 6 are in parentheses. \textsuperscript{e}The (E,E)/(E,Z) ratios of 7 are in parentheses. \textsuperscript{f}The reaction was run at room temperature. \textsuperscript{g}Isolated yield: 98%. \textsuperscript{h}Isolated yield: 97%.
Synthesis of All-trans PpPVs. The synthesis of all-trans 3 in eq 1 was carried out under the reaction conditions based on entries 9, 13, and 15 in Table 1 (Table 2). An 1:1 mixture of (E,E)-1,4-bis(2-bromoethenyl)benzene (1) and 2,5-dioctyloxy-benzene-1,4-diboronic acid (2a) was heated in toluene at 80 °C for 24 h in the presence of [Pd(PPh₃)₄] (1.5 mol%), aqueous NaOH (3 equiv), and Bu₄NBr (1 equiv), giving orange fluorescent suspension, which was diluted with CH₂Cl₂, washed with H₂O, and reprecipitated in methanol (entry 1). ¹H NMR analysis of the resulting polymer revealed a partial diene structure in the main chain (< 5%). On the other hand, the same reaction using [Pd(PBu₃)₂] in place of [Pd(PPh₃)₄] afforded all-trans 3 without a notable defect of the PpPV skeleton (entry 2). The molecular weight decreased in the absence of Bu₄NBr (entry 3), but recovered a comparable level of entry 2 when the reaction was carried out at room temperature using boronic acid 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 slightly warmed conditions (entry 6). Although the reaction was also examined in a refluxed THF solution, the resulting polymer was insoluble in CHCl₃, and therefore could not be fully characterized.

Table 2. Polycondensation of (E,E)-1 with 2

<table>
<thead>
<tr>
<th>entry</th>
<th>Pd cat.</th>
<th>2</th>
<th>Bu₄NBr</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>yield ²</th>
<th>$M_n$ ³</th>
<th>$M_w/M_n$ ³</th>
<th>cis/trans ⁴</th>
<th>defect ⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Pd(PPh₃)₄]</td>
<td>2a</td>
<td>1 equiv</td>
<td>toluene</td>
<td>80</td>
<td>&gt;99</td>
<td>8400</td>
<td>3.03</td>
<td>&lt;1/99</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>[Pd(PBu₃)₂]</td>
<td>2a</td>
<td>1 equiv</td>
<td>toluene</td>
<td>80</td>
<td>&gt;99</td>
<td>4900</td>
<td>2.48</td>
<td>&lt;1/99</td>
<td>none</td>
</tr>
<tr>
<td>3</td>
<td>[Pd(PBu₃)₂]</td>
<td>2a</td>
<td>—</td>
<td>toluene</td>
<td>80</td>
<td>91</td>
<td>2700</td>
<td>1.57</td>
<td>&lt;1/99</td>
<td>none</td>
</tr>
<tr>
<td>4</td>
<td>[Pd(PBu₃)₂]</td>
<td>2b</td>
<td>—</td>
<td>toluene</td>
<td>20</td>
<td>98</td>
<td>4100</td>
<td>1.44</td>
<td>&lt;1/99</td>
<td>none</td>
</tr>
<tr>
<td>5</td>
<td>[Pd(PBu₃)₂]</td>
<td>2b</td>
<td>—</td>
<td>THF</td>
<td>20</td>
<td>&gt;99</td>
<td>7500</td>
<td>1.80</td>
<td>&lt;1/99</td>
<td>none</td>
</tr>
<tr>
<td>6</td>
<td>[Pd(PBu₃)₂]</td>
<td>2b</td>
<td>—</td>
<td>THF</td>
<td>30</td>
<td>&gt;99</td>
<td>9700</td>
<td>1.96</td>
<td>&lt;1/99</td>
<td>none</td>
</tr>
</tbody>
</table>

¹Reactions were carried out for 24 h using (E,E)-1 (0.20 mmol), 2 (0.20 mmol), aqueous NaOH (3.0 M, 0.6 mmol), and Pd catalyst (1.5 mol%) in solution (2.0 mL). ²Yield of MeOH-insoluble polymer. ³Determined by GPC calibration based on polystyrene standards. ⁴Determined by ¹H NMR.
Polycondensation of several \((E,E)\)-bis(2-bromoethenyl)arenes (10–13) with 2b was successful under the optimized catalytic conditions, and thereby four kinds of all-trans PAVs (14–17) were synthesized without notable structural defects (Table 3).

**Table 3.** All-trans PAVs prepared by Polycondensation of \((E,E)\)-BrCH=CH-Ar-CH=CHBr (10–13) with 2b

<table>
<thead>
<tr>
<th>entry</th>
<th>PAV</th>
<th>yield (%)</th>
<th>(M_n)</th>
<th>(M_w/M_n)</th>
<th>cis/trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="attachment" alt="PAV1" /></td>
<td>&gt;99</td>
<td>18300</td>
<td>2.10</td>
<td>&lt;1/99</td>
</tr>
<tr>
<td>2</td>
<td><img src="attachment" alt="PAV2" /></td>
<td>99</td>
<td>9900</td>
<td>2.66</td>
<td>&lt;1/99</td>
</tr>
<tr>
<td>3</td>
<td><img src="attachment" alt="PAV3" /></td>
<td>&gt;99</td>
<td>7600</td>
<td>1.44</td>
<td>&lt;1/99</td>
</tr>
<tr>
<td>4</td>
<td><img src="attachment" alt="PAV4" /></td>
<td>&gt;99</td>
<td>6900</td>
<td>1.17</td>
<td>&lt;1/99</td>
</tr>
</tbody>
</table>

\(^a\)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\(^3\)]_2 (1.5 mol%) in THF (2.0 mL). Ar = \(m\)-phenylene (10), \(o\)-phenylene (11), 4,4’-biphenylene (12), 2,7-fluorenylene (13). \(^b\)Yield of MeOH-insoluble polymer. \(^c\)Determined by GPC calibration based on polystyrene standards. \(^d\)Determined by \(^1\)H NMR.
Characterization of All-trans PpPVs. The polymer structures were characterized 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). It has been shown that the stereoregularity of vinylene linkages can be estimated from the peak intensities of the OCH$_2$ signals of octyloxy groups; the signal of trans-PpPV appears at δ 4.08, whereas that of cis-isomer at δ 3.54. Thus, no trace of the signal of cis-isomer was observed in spectrum (A). As for the terminal structures, the spectrum (A) exhibited the signals assignable to 2,5-dioctyloxyphenyl ((a)–(d)) and (E)-2-bromoethenyl (e) groups in reasonable

![Figure 1](image.png)

**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.
peak intensities. Accordingly, it was concluded that all-trans 3 bears these groups at each terminus.

**Photo-induced Insolubilization of All-trans PpPVs.** A thin film of all-trans 3 ($M_n = 9700$, entry 6 in Table 2) was prepared from a CHCl$_3$ solution (2.0 wt%) by spin-coating on a quartz plate ((i) blue line, $\lambda_{\text{max}} = 478$ nm), irradiated with a Xe lamp ($\lambda = 300–400$ nm, 21.0 mW cm$^{-2}$) for 1 h under vacuum at room temperature ((ii) red line, $\lambda_{\text{max}} = 478$ nm), and rinsed twice with CHCl$_3$ and dried ((iii) green line). Figure 2 shows the UV-vis spectrum at each step. Unlike all-cis PpPVs described in Chapter 1, no notable change was observed before and after UV-irradiation ((i) and (ii)). However, after rinsing, 43% of PpPV film remained on the substrate (iii). Hence, all-trans 3 having a 2-bromoethenyl group at the polymer end was insolubilized under UV light, while the performance was considerably low as compared with all-cis PpPVs (vide infra). It was confirmed that most part of the polymer dissolves in CHCl$_3$.

![Figure 2](image.png)  
**Figure 2.** UV–vis absorption spectra of all-trans 3 ($M_n = 9700$) in thin film, before and after UV-irradiation (i and ii), and after rinsing with CHCl$_3$ (iii).
All-trans Poly(arylenevinylene)s

without UV-irradiation.\textsuperscript{19}

Table 4 compares the performance of all-trans and all-cis 3 on photo-induced insolubilization. The data for all-cis 3 are taken from Chapter 1. It is clearly seen that the performance of all-trans 3 is significantly lower than that of all-cis 3. As pointed out in Chapter 1, all-cis PpPVs are highly mobile molecules in thin films. Accordingly, they may form a highly aligned structure of all-trans PpPVs upon photoisomerization with the aid of attractive interactions between the molecules such as $\pi-\pi$ stacking. In contrast, all-trans 3 should be a highly rigid molecule, and thereby unlikely to undergo molecular alignment in thin films. As an indirect support, the thin films of all-trans 3 remained insulators after photo-irradiation, although those of all-cis 3 exhibited the thin film transistor (TFT) mobility $(\mu_{\text{TFT}})$ of up to $1.6 \times 10^{-4}$ \text{cm}^2 \text{V}^{-1} \text{s}^{-1} upon photo-induced insolubilization.

\begin{table}[h]
\centering
\caption{Photo-induced Insolubilization of PpPVs}
\begin{tabular}{lcccr}
\hline
entry & PPV & $M_n$\textsuperscript{a} & $M_n/M_n$\textsuperscript{a} & insolubilized PpPV (\%)\textsuperscript{b} \\
\hline
1 & all-trans 3 & 2700 & 1.57 & 5 \\
2 & all-trans 3 & 4100 & 1.44 & 10 \\
3 & all-trans 3 & 7500 & 1.80 & 22 \\
4 & all-trans 3 & 9700 & 1.96 & 43 \\
5 & all-cis 3 & 2800 & 1.55 & 33 \\
6 & all-cis 3 & 4800 & 2.20 & 64 \\
7 & all-cis 3 & 7000 & 2.69 & 84 \\
8 & all-cis 3 & 8100 & 3.93 & 89 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Determined by GPC calibration based on polystyrene standards. \textsuperscript{b}Determined by UV–vis absorption spectroscopy.
Conclusions

The author has succeeded in synthesizing all-trans PpPVs and its homologues bearing a 2-bromoethenyl group at the chain end, using Suzuki–Miyaura-type polycondensation of 
(E,E)-bis(2-bromoethenyl)arenes with 2,5-dioctyloxybenzene-1,4-dibronic acid derivatives. Taking the previous mechanistic findings about the homo-coupling of alkenyl bromide into consideration, catalytic cross-coupling systems with perfect selectivity have been developed by pursuit of the reaction conditions. The resulting all-trans PpPVs undergo photo-induced insolubilization, while their performance is much lower than that of all-cis isomers. The present study has provided an additional evidence of the significance of all-cis configuration for the photo-induced insolubilization of PpPV films.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P₂O₅ (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (¹H NMR 400.13 MHz and ¹³C NMR 100.62 MHz). Chemical shifts are reported in δ (ppm), referenced to the ¹H (residual protons) and ¹³C signals of deuterated solvents. Mass spectra were measured on a Shimadzu GC-MS QP2010 spectrometer (EI, 70 eV). Melting points were measured with a Yanaco MP-S3 instrument. 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, 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; Mₙ = 980–1920000). Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PPV was performed with a Mikasa spin coater 1H-DX2. Photo-irradiation 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. The following compounds were synthesized according to literatures: [Pd(PPh3)4], [Pd(PCy3)2], [Pd(PBu(t)3)2], [RuHCl(CO)(PPh3)], (E)-styryl bromide ((E)-4), 2,5-dioctyloxybenzeneboronic acid (5), 2,5-dioctyloxy-1,4-benzenediboronic acid (2a), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (2b), 1-bromo-2,5-dioctyloxybenzene (19), 4,4′-diethynylbiphenyl (20c), and 2,7-diethynylfluorene (20d).

All other chemicals were obtained from commercial suppliers and used without further purification.

Suzuki–Miyaura Cross-coupling of (E)-4 and 5 (run 9 in Table 1). A 10 mL Schlenk tube was charged with 5 (75.7 mg, 0.200 mmol), [Pd(PPh3)4] (3.5 mg, 3.0 µmol), Bu4NBr (64.5 mg, 0.200 mmol), toluene (1 mL), and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). To the resulting suspension was added (E)-4 (36.6 mg, 0.200 mmol). The mixture was stirred at 80 °C for 1 h. After cooling to room temperature, the mixture was passed through a short column (SiO2, hexane/CH2Cl2 (1/1)), concentrated to dryness, and examined by 1H NMR using hexamethylbenzene as an internal standard, showing the formation of (E)-2,5-dioctyloxy stilbene (6, (E)/(Z) > 99/1) in 99% yield, which was isolated as a colorless oil by column chromatography (SiO2, hexane and then hexane/CH2Cl2 (4/1)) (85.7 mg, 98% yield). The NMR data for (E)-6 were identical to those reported. 1H NMR (CDCl3): δ 7.52 (d, J = 7.5 Hz, 2H, H2 of C6H3), 7.46 (d, J = 16.5 Hz, 1H, C6H3CH=CH), 7.35 (t, J = 7.7 Hz, 2H, H3 of C6H3), 7.24 (t, J = 7.5 Hz, 1H, H4 of C6H3), 7.15 (d, J = 3.0 Hz, 1H, H6 of C6H3), 7.11 (d, J = 16.5 Hz, 1H, C6H3CH=CH), 6.82 (d, J = 8.9 Hz, 1H, H3 of C6H3), 6.77 (dd, J = 8.9, 2.9 Hz, 1H, H4 of C6H3), 3.96 (t, J = 6.5 Hz, 2H, OCH2), 3.95 (t, J = 6.5 Hz, 2H, OCH2), 1.87–1.73 (m, 4H, CH2), 1.54–1.23 (m, 20H, CH2), 0.93–0.84 (m, 6H, CH3).
Synthesis of 2,2′,5,5′-tetraoctyloxybiphenyl (8).

![Chemical structure](image)

To a solution of 1-bromo-2,5-dioctyloxybenzene (19) (207 mg, 0.500 mmol) and 5 (208 mg, 0.550 mmol) in toluene (5 mL) were successively added [Pd(PBu₃)₂] (2.8 mg, 5.0 µmol) and 3.0 M aqueous KOH (0.50 mL, 1.5 mmol). The mixture was stirred at 80 °C for 12 h, and passed through a short column (SiO₂, hexane/CH₂Cl₂ (1/1)) at room temperature. Purification of the crude product by flash column chromatography (SiO₂, hexane and then hexane/CH₂Cl₂ (2/1)) gave the title compound as a white solid (331.6 mg, 99% yield). Mp: 46–48 °C. ¹H NMR (CDCl₃): δ 6.86 (d, J = 6.3 Hz, 2H, H₃,₃′ of Ar), 6.84 (s, 2H, H₆,₆′ of Ar), 6.80 (dd, J = 8.7, 2.8 Hz, 2H, H₄,₄′ of Ar), 3.90 (t, J = 6.6 Hz, 4H, OCH₂), 3.81 (t, J = 6.5 Hz, 4H, OCH₂), 1.78–1.70 (m, 4H, CH₂), 1.49–1.17 (m, 40H, CH₂), 0.91–0.84 (m, 12H, CH₃). ¹³C{¹H}NMR (CDCl₃): δ 152.8 (s, C₅,₅′ of Ar), 150.7 (s, C₂,₂′ of Ar), 129.3 (s, C₁,₁′ of Ar), 117.7 (s, C₃,₃′ of Ar), 114.3 (s, C₄,₄′ and C₆,₆′ of Ar), 69.7, 68.6 (each s, OCH₂), 31.8, 31.8, 29.4, 29.4, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7 (each s, CH₂), 14.1 (s, CH₃). Anal. Calcd. for C₄₄H₇₄O₄: C, 79.22; H, 11.18. Found: C, 79.61; H, 11.28.

Synthesis of (E,E)-Bis(2-bromoethyl)arenes (1, 10, 12 and 13). These compounds were prepared by a two-step procedure.
(i) (E,E)-Bis[2-(dimethylphenylsilyl)ethenyl]arene (21a–d).

A typical procedure is reported for (E,E)-21a. To a solution of HSiMe₂Ph (1.9 mL, 12 mmol) and 1,4-diethynylbenzene (20a; 316 mg, 2.50 mmol) in CH₂Cl₂ (10 mL) was added [RuHCl(CO)(PPh₃)₃] (238 mg, 0.250 mmol). The mixture was stirred for 2 h at room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, hexane and then hexane/CH₂Cl₂ (9/1)), and (E,E)-21a ((E,E) > 99/1) was isolated as a white solid (877 mg, 88% yield). Similarly, compounds (E,E)-21b, 21c, and 21d were synthesized from the corresponding diethynylarene (20b–d) in 95, 96, and 85% yields, respectively.

(E,E)-21a. White solid. Mp: 93–94 °C. ¹H NMR (CDCl₃): δ 7.60–7.54 (m, 4H, o- and p-Ph), 7.40 (s, 4H, Ar), 7.39–7.34 (m, 6H, o- and p-Ph), 7.40 (s, 4H, Ar), 6.71 (d, J = 19.1 Hz, 2H, ArCH=), 6.58 (d, J = 19.1 Hz, 2H, =CHSi), 0.43 (s, 12H, Si(CH₃)₂). ¹³C{¹H}NMR (CDCl₃): δ 144.8 (s, ArCH=), 138.5 (s, ipso-C of Ph), 138.0 (s, C¹,4 of Ar), 133.9 (s, o-C of Ph), 129.1 (s, p-C of Ph), 127.8 (s, m-C of Ph), 127.3 (s, =CHSi), 126.7 (s, C²,3,5,6 of Ar), –2.5 (s, Si(CH₃)₂). Anal. Calcd. for C₂₆H₃₀Si₂: C, 78.33; H, 7.58. Found: C, 78.31; H, 7.59.

(E,E)-21b. Purified by flash column chromatography (SiO₂, hexane). Colorless oil. ¹H NMR (CDCl₃): δ 7.60–7.54 (m, 4H, m-Ph), 7.53 (s, 1H, H² of Ar), 7.39–7.32 (m, 8H, o- and p-Ph and H⁴,⁶ of Ar), 7.28 (dd, J = 8.7, 6.2 Hz, 1H, H⁵ of Ar), 6.93 (d, J = 19.1 Hz, 2H, ArCH=), 6.60 (d, J = 19.1 Hz, 2H, =CHSi), 0.43 (s, 12H, Si(CH₃)₂). ¹³C{¹H}NMR (CDCl₃): δ 145.1 (s, ArCH=), 142.3 (s, C¹ of Ph), 138.5, 138.4 (each s, ipso-C of Ph and C¹,3 of Ar), 133.9 (s, o-C of Ph), 129.1 (s, p-C of Ph), 128.7 (s, C⁵ of Ar), 127.8 (s, m-C of Ph), 127.5 (s, =CHSi), 126.3 (s, C⁴,⁶ of Ar), 124.6 (s, C² of Ar), –2.5 (s, Si(CH₃)₂). Anal. Calcd. for C₂₆H₳₃Si₂: C, 78.33; H, 7.58. Found: C, 78.48; H, 7.59.

(E,E)-21c. Purified by flash column chromatography (SiO₂, hexane/CH₂Cl₂ (9/1)). White solid. Mp: 121–123 °C. ¹H NMR (CDCl₃): δ 7.61–7.54 (m, 4H, m-Ph), 7.58, 7.51 (each d, J = 8.3 Hz, 4H, C₆H₄), 7.40–7.34 (m, 6H, o- and p-Ph), 6.97 (d, J = 19.1 Hz, 2H, C₆H₄CH=), 6.62 (d, J = 19.1 Hz, 2H, =CHSi), 0.45 (s, 12H, Si(CH₃)₂). ¹³C{¹H}NMR (CDCl₃): δ 144.7 (s, C₆H₄CH=), 140.3 (s, C¹ of C₆H₄), 138.5 (s, ipso-C of Ph), 137.3 (C⁴ of
Chapter 5

C₆H₄), 133.9 (s, o-C of Ph), 129.1 (s, p-C of Ph), 127.8 (s, m-C of Ph), 127.4 (s, =CHSi), 127.0, 127.0 (each s, C², and C³ of C₆H₄), -2.5 (s, Si(CH₃)₂). Anal. Calcd. for C₃₂H₃₄Si₂: C, 80.95; H, 7.22. Found: C, 80.98; H, 7.18.

(E,E)-21d. Purified by flash column chromatography (SiO₂, hexane/CH₂Cl₂ (9/1)). White solid. Mp: 106–108 °C. ¹H NMR (CDCl₃): δ 7.70 (d, J = 7.9 Hz, 2H, H₄,5 of Fl), 7.63 (br s, 2H, H₁,8 of Fl), 7.62–7.57 (m, 4H, m-Ph), 7.44 (d, J = 7.9 Hz, 2H, H₃,6 of Fl), 3.86 (s, 2H, CH₂), 0.45 (s, 12H, Si(CH₃)₂). ¹³C{¹H}NMR (CDCl₃): δ 145.5 (s, FlCH=), 144.0, 141.5 (each s, Fl), 138.7 (s, ipso-C of Ph), 137.0 (s, Fl), 133.9 (s, o-C of Ph), 129.0 (s, p-C of Ph), 127.8 (s, m-C of Ph), 126.5 (s, =CHSi), 36.7 (s, CH₂), -2.5 (s, Si(CH₃)₂). Anal. Calcd. for C₃₃H₃₄Si₂: C, 81.42; H, 7.04. Found: C, 81.53; H, 7.12.

(ii) (E,E)-Bis(2-bromoethenyl)arene (1, 10, 12 and 13).²⁹ A typical procedure is reported for (E,E)-1 (Ar = p-phenylene). To a solution of (E,E)-21a (598 mg, 1.50 mmol) in CH₃CN (60 mL) was added N-bromosuccinimide (1.07 g, 6.00 mmol) at room temperature, and the mixture was stirred for 3 h. 10% aqueous Na₂S₂O₃ solution (100 mL) was added, and the mixture was extracted with CHCl₃ (4 × 75 mL). The combined extracts were washed with 1 N aqueous NaOH (2 × 100 mL) and brine (100 mL), dried over MgSO₄, concentrated under reduced pressure. The crude product was recrystallized from Et₂O/MeOH at −30 °C to give (E,E)-1 (>99% purity) as a white solid (311 mg, 72% yield). Similarly, (E,E)-10 (Ar = m-phenylene), 12 (Ar = 4,4'-biphenylene), and 13 (Ar = 2,7-fluorenylene) were synthesized from (E,E)-21b–d in 56, 96, and 88% yields, respectively.

(E,E)-1. White solid. Mp: 139–141 °C. ¹H NMR (CDCl₃): δ 7.25 (s, 4H, Ar), 7.07 (d, J = 14.0 Hz, 2H, ArCH=), 6.79 (d, J = 14.0 Hz, 2H, =CHBr). ¹³C{¹H}NMR (CDCl₃): δ 136.6 (s, ArCH=), 135.7 (s, C¹,4 of Ar), 126.5 (s, C²,3,5,6 of Ar), 107.1 (s, =CHBr). MS, m/z (relative intensity, %): 291 (M⁺ + 3, 5), 290 (M⁺ + 2, 42), 289 (M⁺ + 1, 10), 288 (M⁺, 88), 286 (M⁺ – 1, 46), 209 (31), 207 (32), 129 (10), 128 (100), 127 (43), 126 (17), 103 (10), 102 (27), 101 (16), 77 (21), 76 (17), 75 (24), 74 (15), 64 (22), 63 (42), 52 (10), 51 (39), 50 (20). Anal. Calcd. for C₁₀H₃Br₂: C, 41.71; H, 2.80. Found: C, 41.63; H, 2.88.

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(E,E)-10. Recrystallized from Et₂O/MeOH at –70 °C. White solid. Mp: 45 °C. 1H NMR (CDCl₃): δ 7.29 (dd, J = 8.6, 6.5 Hz, 1H, H₅ of Ar), 7.23 (s, 1H, H² of Ar), 7.21 (d, J = 7.6 Hz, 2H, H⁴,⁶ of Ar), 7.08 (d, J = 14.0 Hz, 2H, ArCH=), 6.79 (d, J = 14.0 Hz, 2H, =CHBr). 13C{¹H} NMR (CDCl₃): δ 136.6 (s, ArCH=), 136.5 (s, C¹,³ of Ar), 129.3 (s, C⁵ of Ar), 125.8 (s, C⁴,⁶ of Ar), 123.9 (s, C² of Ar), 107.4 (s, =CHBr). MS, m/z (relative intensity, %): 291 (M⁺ + 3, 5), 290 (M⁺ + 2, 40), 289 (M⁺ + 1, 10), 288 (M⁺, 87), 286 (M⁺ – 1, 42), 209 (19), 207 (20), 129 (12), 128 (100), 127 (29), 126 (12), 104 (17), 103 (14), 102 (25), 101 (13), 77 (21), 76 (19), 75 (26), 74 (17), 64 (48), 63 (71), 62 (10), 52 (10), 51 (80), 50 (40). Anal. Calcd. for C₁₀H₈Br₂: C, 41.71; H, 2.80. Found: C, 41.79; H, 2.74.

(E,E)-11. Recrystallized from THF/MeOH at –30 °C. White solid. Mp: 217–219 °C. 1H NMR (CDCl₃): δ 7.56, 7.37 (each d, J = 8.3 Hz, 4H, C₆H₄), 7.14 (d, J = 14.0 Hz, 2H, C₆H₄CH=), 6.82 (d, J = 14.0 Hz, 2H, =CHBr). 13C{¹H} NMR (CDCl₃): δ 140.2 (s, C¹ of C₆H₄), 136.7 (s, C₆H₄CH=), 135.1 (C⁴ of C₆H₄), 127.2, 126.6 (each s, C²,⁶ and C³,⁵ of C₆H₄), 106.8 (s, =CHBr). MS, m/z (relative intensity, %): 367 (M⁺ + 3, 8), 366 (M⁺ + 2, 52), 365 (M⁺ + 1, 18), 364 (M⁺, 100), 363 (M⁺ – 1, 9), 362(M⁺ – 2, 52), 285 (11), 283 (11), 204 (20), 203 (28), 202 (55), 176 (15), 151 (10), 102 (42), 101 (44), 100 (12), 89 (20), 88 (27), 76 (25), 75 (15), 63 (10). Anal. Calcd. for C₁₆H₁₂Br₂: C, 52.78; H, 3.32. Found: C, 52.98; H, 2.20.

(E,E)-13. Recrystallized from CH₂Cl₂/MeOH at –30 °C. White solid. Mp: 204–206 °C. 1H NMR (CDCl₃): δ 7.70 (d, J = 7.9 Hz, 2H, H⁴,⁵ of Fl), 7.48 (br s, 2H, H¹,³ of Fl), 7.32 (d, J = 7.9 Hz, 2H, H³,⁵ of Fl), 7.17 (d, J = 14.0 Hz, 2H, FlCH=), 6.82 (d, J = 14.0 Hz, 2H, =CHBr), 3.90 (s, 2H, CH₂). 13C{¹H} NMR (CDCl₃): δ 144.1, 141.4 (each s, Fl), 137.4 (s, FlCH=), 134.7, 125.4, 122.6, 120.3 (each s, Fl), 106.0 (s, =CHBr), 36.7 (s, CH₂). MS, m/z (relative intensity, %): 379 (M⁺ + 3, 8), 378 (M⁺ + 2, 45), 377 (M⁺ + 1, 18), 376 (M⁺, 88), 375 (M⁺ – 1, 10), 374 (M⁺ – 2, 46), 297 (13), 295 (18), 217 (15), 216 (79), 215 (100), 214 (15), 213 (32), 190 (13), 189 (49), 188 (17), 187 (19), 163 (10), 149 (14), 108 (32), 107 (78), 106 (13), 95 (32), 95 (70), 94 (12), 82 (16). Anal. Calcd. for C₁₇H₁₂Br₂: C, 54.29; H, 3.22. Found: C, 54.26; H, 3.24.
Synthesis of \((E, E)\)-Bis-1,2-(2-bromoethenyl)benzene (12).

\[ \text{CHO} \quad \begin{array}{c} \text{CBr}_4 \\ \text{PPh}_3 \\ \text{CH}_2\text{Cl}_2 \end{array} \quad \begin{array}{c} \text{CHO} \\ \text{Br} \\ \text{Br} \\ \text{Br} \\ \text{Br} \\ \text{(EtO)}_2\text{P(O)H} \\ \text{Et}_3\text{N} \end{array} \quad \begin{array}{c} \text{CHO} \\ \text{Br} \\ \text{Br} \end{array} \]

This compound was prepared by a two-step procedure.\(^{30}\) (i) A solution of \(\text{CBr}_4\) (14.6 g, 44.0 mmol) in \(\text{CH}_2\text{Cl}_2\) (44 mL) was added dropwise to a solution of \(o\)-phthalaldehyde (22; 2.68 g, 20.0 mmol) and \(\text{PPh}_3\) (22.0 g, 84.0 mmol) in \(\text{CH}_2\text{Cl}_2\) (100 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, purified by column chromatography (SiO\(_2\), hexane), giving bis-1,2-(2,2-dibromoethenyl)benzene (23) as an orange oil (8.04 g, 90% yield). The NMR data were identical to those reported.\(^{31}\) \(^{1}\)H NMR (CDCl\(_3\)): \(\delta 7.53–7.49\) (m, 2H, H\(_{3,6}\) of Ar), 7.42 (s, 2H, CH=CBr\(_2\)), 7.40–7.35 (m, 2H, H\(_{4,5}\) of Ar).

(ii) A mixture of 23 (4.46 g, 10.0 mmol), diethyl phosphite (9.0 mL, 70 mmol), and \(\text{Et}_3\text{N}\) (14 mL, 100 mmol) was stirred under reflux for 5 h. The reaction mixture was cooled to room temperature, poured into 1 N aqueous HCl (100 mL), and extracted with \(\text{CH}_2\text{Cl}_2\) (4 × 50 mL). The combined extracts were washed with brine (100 mL), dried over MgSO\(_4\), and concentrated under reduced pressure. The resulting solid was purified by flash column chromatography (SiO\(_2\), hexane) and then by recrystallization from \(\text{CH}_2\text{Cl}_2\)/hexane at −30 °C, giving colorless crystals of \((E, E)\)-12 (1.59 g, 55% yield). Mp: 66–68 °C. \(^{1}\)H NMR (CDCl\(_3\)): \(\delta 7.33–7.26\) (m, 4H, Ar), 7.31 (d, \(J = 13.8\) Hz, 2H, ArCH=), 6.67 (d, \(J = 13.8\) Hz, 2H, =CHBr). \(^{13}\)C\({}^{1}\)H\(_3\) NMR (CDCl\(_3\)): \(\delta 134.9\) (s, ArCH=), 133.9 (s, C\(_{1,2}\) of Ar), 128.6, 127.0 (each s, C\(_{3,6}\) and C\(_{4,5}\) of Ar), 109.0 (s, =CHBr). MS, \(m/z\) (relative intensity, %): 288 (M\(^+\), 1), 209 (4), 207 (4), 129 (11), 128 (100), 127 (10), 126 (4), 102 (5), 77 (5), 76 (3), 75 (5), 64 (6), 63 (10), 51 (8), 50 (4). Anal. Calcd. for C\(_{10}\)H\(_8\)Br\(_2\): C, 41.71; H, 2.80. Found: C, 42.00; H, 2.79.

Synthesis of All-trans PpPV (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), \(\text{Bu}_4\text{NBr}\) (64.5 mg, 0.200 mmol), toluene
All-trans Poly(arylenevinylene)s

(2 mL) and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). [Pd(PBu₃)₂] (1.5 mg, 3.0 µmol) was added, and the mixture was stirred at 80 °C for 24 h. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (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).

¹H NMR (CDCl₃): δ 7.53 (s, C₆H₄), 7.50 (d, J = 16.5 Hz, CH=CH), 7.50–7.45 (m, H⁵,₆ of terminal C₆H₄CH=CHBr), 7.30 (d, J = 8.6 Hz, H³,₅ of terminal C₆H₄CH=CHBr), 7.15 (d, J = 16.7 Hz, CH=CH), 7.14 (s, H³,₆ of C₆H₂), 7.11 (d, J = 14.2 Hz, CH=CHBr of terminal C₆H₄CH=CHBr), 6.83 (d, J = 9.1 Hz, H³ of terminal C₆H₃(OC₈H₁₇)₂), 6.79 (d, J = 14.0 Hz, 1H, CH=CHBr), 6.77 (dd, J = 8.9, 2.8 Hz, H⁴ of terminal C₆H₃(OC₈H₁₇)₂), 4.08 (t, J = 6.0 Hz, OCH₂), 3.98 and 3.96 (t, J = 6.3 Hz, OCH₂ of terminal C₆H₃(OC₈H₁₇)₂), 1.96–1.80 and 1.62–1.18 (m, CH₂), 0.92–0.80 (m, CH₃).

¹³C{¹H} NMR (CDCl₃): δ 151.2 (s, C²,₅ of C₆H₄), 137.2 (s, C¹,₄ of C₆H₄), 128.5 (s, CH=CH), 127.0 (s, C¹,₂ of C₆H₂), 126.8 (s, C²,₃,₅,₆ of C₆H₄), 123.2 (s, CH=CH), 110.6 (s, C³,₆ of C₆H₂), 69.6 (s, OCH₂), 31.8, 29.5, 29.4, 29.3, 26.3, 22.7 (each s, CH₂), 14.1 (s, CH₃).

Synthesis of All-trans PAVs (14–17). These polymers were synthesized similarly to all-trans PpPV (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(PBu₃)₂] (1.5 mg, 3.0 µmol) at room temperature for 24 h.

All-trans 14. Yellow solid. ¹H NMR (CDCl₃): δ 7.65 (s, H² of C₆H₄), 7.54 (d, J = 16.3 Hz, CH=CH), 7.48 (d, J = 7.5 Hz, H¹,₆ of C₆H₄), 7.38 (t, J = 7.3 Hz, H² of C₆H₄), 7.22–7.13 (m, H¹,₆ of C₆H₂ and CH=CH), 4.10 (t, J = 6.0 Hz, OCH₂), 1.96–1.83 and 1.63–1.18 (m, CH₂), 0.92–0.80 (m, CH₃).

¹³C{¹H} NMR (CDCl₃): δ 151.2 (s, C²,₅ of C₆H₂), 138.3 (s, C¹,₃ of C₆H₄), 128.9 (s, CH=CH), 127.0 (s, C¹,₂ of C₆H₂), 125.5, 125.3 (each s, C² and C⁶ of C₆H₄), 123.8 (s, CH=CH), 110.9 (s, C³,₆ of C₆H₂), 69.7 (s, OCH₂), 31.8, 29.5, 29.4, 29.4, 26.3, 22.7 (each s, CH₂), 14.1 (s, CH₃).
All-trans 15. Yellow solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta 7.70–7.58 \text{ (m, C}_6\text{H}_4\), 7.37 \text{ (d, } J = 16.2 \text{ Hz, CH=CH), 7.32–7.22 \text{ (m, C}_6\text{H}_4\), 7.12 \text{ (s, H}^{3,6} \text{ of C}_6\text{H}_2\), 3.99 \text{ (t, } J = 6.3 \text{ Hz, OCH}_2\), 1.83–1.68 and 1.50–1.12 \text{ (m, CH}_2\), 0.90–0.77 \text{ (m, CH}_3\).

\(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta 151.2 \text{ (s, C}_2,5\text{ of C}_6\text{H}_2\), 136.7 \text{ (s, C}_1,2\text{ of C}_6\text{H}_4\), 127.5 \text{ (s, CH=CH), 127.2 \text{ (s, C}^{1,4}\text{ of C}_6\text{H}_2\), 126.9, 126.8, 126.1 \text{ (each s, C}^{3,6}\text{ and C}^{4,5}\text{ of C}_6\text{H}_4\) and CH=CH), 110.8 \text{ (s, C}_3,6\text{ of C}_6\text{H}_2\), 69.5 \text{ (s, OCH}_2\), 31.8, 29.5, 29.4, 29.4, 26.3, 22.7 \text{ (each s, CH}_2\), 14.1 \text{ (s, CH}_3\).

All-trans 16. Yellow solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta 7.70–7.48 \text{ (m, C}_6\text{H}_4\), 7.55 \text{ (d, } J = 16.3 \text{ Hz, CH=CH), 7.19 \text{ (d, } J = 16.3 \text{ Hz, CH=CH), 7.17 \text{ (s, H}^{3,6} \text{ of C}_6\text{H}_2\), 4.09 \text{ (t, } J = 6.3 \text{ Hz, OCH}_2\), 1.96–1.80 and 1.63–1.18 \text{ (m, CH}_2\), 0.94–0.82 \text{ (m, CH}_3\).

\(^{13}\)C\{\(^1\)H\} NMR analysis was not feasible due to low solubility.

All-trans 17. Orange solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta 7.83–7.68 \text{ and 7.62–7.46 \text{ (m, Fl), 7.55 \text{ (d, } J = 16.0 \text{ Hz, CH=CH), 7.24–7.10 \text{ (m, H}^{3,6} \text{ of C}_6\text{H}_2 \text{ and CH=CH), 4.10 }\text{ (t, } J = 6.3 \text{ Hz, OCH}_2\), 1.97–1.81 \text{ and 1.65–1.18 \text{ (m, CH}_2\), 0.96–0.82 \text{ (m, CH}_3\).

\(^{13}\)C\{\(^1\)H\} NMR analysis was not feasible due to low solubility.

Synthesis of \((E,E)-2,5\)-Dioctyloxy-4’-(2-bromoethenyl)stilbene (18).

![Synthesis of \((E,E)-2,5\)-Dioctyloxy-4’-(2-bromoethenyl)stilbene (18).](attachment:image)

To a solution of \((E,E)-1\) (130 mg, 0.450 mmol) and 5 (114 mg, 0.300 mmol) in toluene (1.5 mL) were successively added [Pd(PBu\(_3\))\(_2\)] (2.3 mg, 4.5 \(\mu\)mol) 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\(_2\)Cl\(_2\) (1/1)), and purified by flash column chromatography (SiO\(_2\), hexane and then hexane/CH\(_2\)Cl\(_2\) (10/1)), giving the title compound as a yellow solid (89.2 mg, 55% yield). M\(\text{p: 44–46 °C. \(^1\)H NMR (CDCl}\(_3\)): \(\delta 7.47 \text{ (d, } J = 16.3 \text{ Hz, 1H, C}_6\text{H}_3\text{CH=CH), 7.46 \text{ (d, } J = 8.3 \text{ Hz, 2H, H}^{2,5}\text{ of C}_6\text{H}_4\), 7.28 \text{ (d, } J = 8.2 \text{ Hz, 2H, H}^{3,6}\text{ of C}_6\text{H}_4\), 7.13 \text{ (d, } J = 3.7 \text{ Hz, 1H, H}^6 \text{ of C}_6\text{H}_3\), 7.10 \text{ (d, } J = 14.0.
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7.07 (d, $J = 16.5$ Hz, 1H, C$_6$H$_3$CH=CH), 6.83 (d, $J = 8.9$ Hz, 1H, H$^3$ of C$_6$H$_3$), 6.78 (d, $J = 13.9$ Hz, 1H, CH=CHBr), 6.78 (dd, $J = 9.1$, 2.8 Hz, 1H, H$^4$ of C$_6$H$_3$), 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($^1$H)NMR (CDCl$_3$): δ 153.3, 151.0 (each s, C$_2,5$ of C$_6$H$_3$), 138.0, 134.8 (each s, C$^{1,4'}$ of C$_6$H$_4$), 136.9 (s, CH=CHBr), 128.3 (s, CH=CH), 127.3 (s, C$^1$ of C$_6$H$_3$), 126.9, 126.4 (each s, C$^{2,3',5',6'}$ of C$_6$H$_4$), 124.1 (s, CH=CH), 114.7, 113.9, 112.3 (each s, C$^{3,4,6'}$ of C$_6$H$_3$), 106.2 (s, CH=CHBr), 69.5, 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, 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.

**Photo-induced Insolubilization of PpPV.** A solution of PpPV 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 PpPV 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 then 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 ($\lambda_{\text{max}} = 365$ 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.

**Measurement of Carrier Mobility.** All manipulations were carried out in an argon-filled glove box. An OFET device was fabricated in a top-contact configuration on a $p$-type Si wafer as a gate electrode (one-side polished, < 0.02 Ω resistance, Furuuchi Chemical Co.) with 3000-Å-thick SiO$_2$ ($C_i = 11$ nF cm$^{-2}$) as a dielectric film. A plate was cut and washed in 2-propanol under ultrasonic wave and under boiling. A thin film of PpPVs as
the active layer (ca. 30 nm thick) was deposited on the Si/SiO\textsubscript{2} substrate by spin-coating a 0.1–0.5 wt\% solution in CHCl\textsubscript{3} at 100–8000 rpm for 60 s, and dried under vacuum at room temperature, and irradiated by a Xe lamp (λ\textsubscript{max} = 365 nm, 23.0 mW cm\textsuperscript{-2}) for 1 h. On the top of the thin film, gold films (30 nm) as source and drain electrodes were deposited through a mask. A drain-source channel length (\(L\)) and width (\(W\)) were 20 µm and 5 mm, respectively. Characteristics of OFET devices were evaluated at room temperature with two source meters (2400, Keithley Instruments Inc.). Carrier mobility (\(\mu\textsubscript{FET}\)) was calculated in the saturation regime (\(V\textsubscript{d} = 100\) V) of the \(I\textsubscript{d}\) using the following equation,

\[
I\textsubscript{d} = (WC/2L) \mu\textsubscript{FET} (V\textsubscript{g} - V\textsubscript{t})^2
\]

where \(C\) is the capacitance of the SiO\textsubscript{2} insulator, and \(V\textsubscript{g}\) and \(V\textsubscript{t}\) are the gate and threshold voltages, respectively. In another case, the PPV thin film was rinsed twice with toluene (1 mL) after UV-irradiation, and examined in a similar manner.

References and notes


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(17) All-trans PpPV ($M_n = 7200, M_w/M_n = 1.81$), prepared by Hiyama-type polycondensation of 2,5-dioctyloxy-1,4-diiodobenzene with ($E,E$)-bis(2-silylethenyl)benzene, scarcely remained on a quartz substrate (8%) after UV-irradiation ($\lambda_{\text{max}} = 365$ nm, 21.0 mW cm$^{-2}$) on a thin film for 1 h at room temperature, followed by rinsing twice with CHCl$_3$.


(19) A spin-coated film of all-trans 3 ($M_n = 9700$) on a quartz substrate was allowed to stand for 1 h at room temperature under vacuum in the dark. After rinsing the film twice with CHCl$_3$, 6% of PpPV remained on the substrate as confirmed by UV-vis absorption spectroscopy.


Chapter 5

List of Publications

General Introduction

“Structure-Controlled Synthesis of π-Conjugated Polymers by Means of Transition-Metal Catalysts”
Masayuki Wakioka, Ryo Takita, and Fumiyuki Ozawa

Chapter 1

“Effects of Primary Structures on Photo-induced Insolubilization of Poly(phenylenevinylene)s in Thin Films”
Yuichiro Mutoh, Yasutaka Yamamoto, Masayuki Wakioka, Ryo Takita, Jun-ichi Nakamura, Toshiya Iida, and Fumiyuki Ozawa

Chapter 2

“Stereocntrolled Synthesis and Photochemical Properties of All-cis and All-trans Poly(m-phenylenevinylene)s”
Masayuki Wakioka, Yasutaka Yamamoto, and Fumiyuki Ozawa

Chapter 3

“Reaction of trans-Pd(styrryl)Br(PMePh$_2$)$_2$ with Styryl Bromide Affording 1,4-Diphenylbutadiene. An Unexpected Homo-Coupling Process Induced by P–C Reductive Elimination”
Masayuki Wakioka, Masato Nagao, and Fumiyuki Ozawa
List of Publications

Chapter 4

“Mechanism of C–P Reductive Elimination from \( trans-[\text{Pd}(\text{CH}=\text{CHPh})\text{Br}(\text{PMePh}_2)_2] \)”
Masayuki Wakioka, Yumiko Nakajima, and Fumiyuki Ozawa

Chapter 5

“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

Other Publication

“Stereocontrolled Synthesis and Characterization of All-cis Poly(arylenevinylene)s”
Hiroyuki Katayama, Masato Nagao, Tatsuro Nishimura, Yukio Matsui, Yosuke Fukuse, Masayuki Wakioka, and Fumiyuki Ozawa

“Possibility of Living Radical Polymerization of Vinyl Acetate Catalyzed by Iron(I) Complex”
Masayuki Wakioka, Kyung-Youl Baek, Tsuyoshi Ando, Masami Kamigaito, and Mitsuo Sawamoto
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