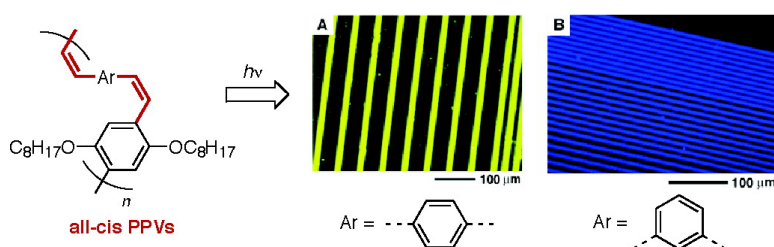


Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs

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Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs

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Abstract: Geometrically pure, all-cis poly(phenylene vinylenes) (PPVs) are synthesized by Suzuki–Miyaura-type polycondensation of 2,5-dioctyloxy-1,4-benzenediboric acid with (*Z,Z*)-bis(2-bromoethenyl)benzenes, which are prepared by ruthenium-catalyzed (*Z*)-selective double hydrosilylation of diethynylbenzenes, followed by bromodesilylation of the resulting (*Z,Z*)-bis(2-silylethenyl)benzenes with *N*-bromosuccinimide. The all-cis PPVs thus obtained undergo one-way photoisomerization to the corresponding *trans*-PPVs both in solution and in the solid. This phenomenon is applied to direct microscale patterning of PPVs onto a quartz substrate.

Poly(phenylene vinylenes) (PPVs) belong to the group of π -conjugated polymers that have applications in light-emitting diodes (LEDs),^{1,2} lasers,³ and solar cells.⁴ Considerable efforts have been made to improve their emission color and efficiency in LEDs by introducing substituents to the polymer skeletons. On the other hand, although stereoregularity of vinylenic linkages in the polymer backbone is also known to profoundly affect the optical properties of PPVs,⁵ efficient ways of regulating the geometries of vinylenic linkages have remained almost unexplored. It is particularly difficult to prepare geometrically pure

all-cis PPVs using previous polymerization methods based on Gilch, Heck, and Wittig reactions.

We recently examined a stereocontrolled synthesis of *trans*- and *cis*-PPVs using Hiyama-type polycondensations of 2,5-dioctyloxy-1,4-diiodobenzene with (*E,E*)- and (*Z,Z*)-1,4-bis(2-silylethenyl)benzenes.⁶ All-*trans* PPV was successfully prepared by this method, but stereoregularity for *cis*-PPV was limited to 66%. Herein, we report that all-cis PPVs are synthesized by Suzuki–Miyaura coupling.⁷ The resulting polymers exhibit a rather unique photochemical property that allows the direct microscale patterning of PPVs onto a quartz substrate.

Results and Discussion

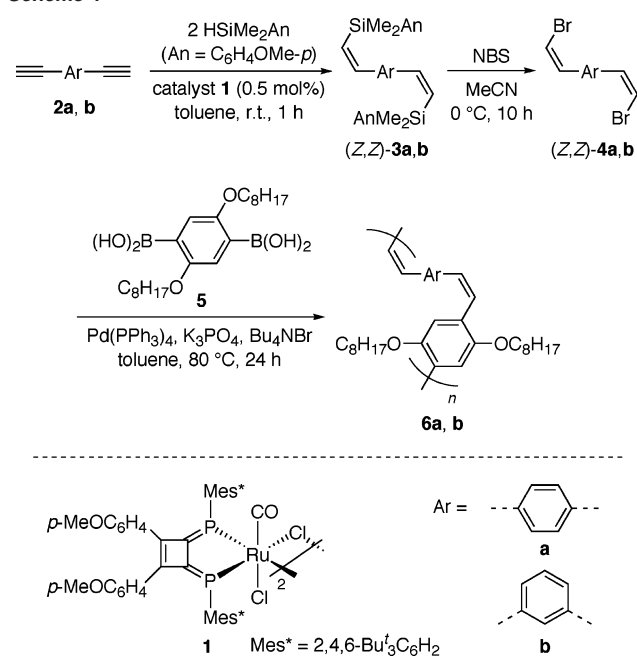
The PPV synthesis was performed with *p*- and *m*-isomers of (*Z,Z*)-bis(2-bromoethenyl)benzene (**4a,b**) as monomers, which were prepared by a two-step procedure given in Scheme 1.⁸ The first step is (*Z*)-selective double hydrosilylation of 1,4- and

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Scheme 1



1,3-diethynylbenzenes (**2a,b**) with HSiMe₂An (An = 4-methoxyphenyl) to give (Z,Z)-1,4- and (Z,Z)-1,3-bis(2-silylethenyl)benzenes (**3a,b**), respectively. While this reaction was previously carried out with RuCl₂(CO)(PPR'₃)₂ (10 mol %) as a catalyst in 91–92% selectivities,⁶ it was found that a newly prepared ruthenium complex **1** bearing an sp²-hybridized phosphorus ligand (DPCB-OMe)⁹ serves as a more efficient catalyst with higher reactivity and selectivity.^{10–12} Thus, the reaction of **2a** with HSiMe₂An (1.9 equiv) in toluene, in the presence of 0.5 mol % of **1**, was complete in 1 h at room temperature to give (Z,Z)-**3a** in over 99% regio- and stereoselectivities. Treatment of the product with *N*-bromosuccinimide (NBS) in acetonitrile at 0 °C formed (Z,Z)-**4a** in 65% yield (two steps).¹³ The *m*-isomer (Z,Z)-**4b** was similarly prepared from **2b** in 56% yield. Complex **1** was prepared in 49% yield by treatment of Ru(η^3 -allyl)Cl(CO)₃¹⁴ with DPCB-OMe in toluene, followed by treatment with dry HCl in ether (see Supporting Information).

Polycondensation of (Z,Z)-**4a** with 1 equiv of 2,5-dioctyloxy-1,4-benzenediboronic acid (**5**) was performed in toluene at 80 °C for 24 h in the presence of Pd(PPh₃)₄ (1.5 mol %), Bu₄-

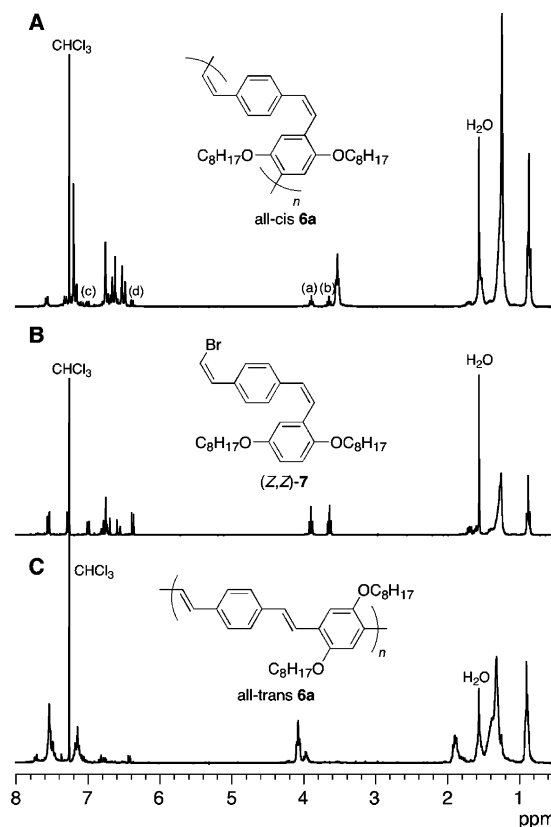


Figure 1. ¹H NMR spectra of all-cis **6a** ($M_n = 2700$) (A), (Z,Z)-**7** (B), and all-trans **6a** obtained by photoisomerization (C).

NBr (1 equiv), and aqueous K₃PO₄ (3 equiv). The reaction solution was then poured into excess MeOH to precipitate an orange solid of all-cis PPV **6a** ($M_n = 4700$, PDI = 1.92, 95% yield).¹⁵ Similarly, all-cis **6b** ($M_n = 5100$, PDI = 2.13) was obtained in 99% yield, starting from (Z,Z)-**4b** and **5**. All procedures must be performed in the dark to avoid cis-to-trans isomerization of PPVs (vide infra). The use of KOH instead of K₃PO₄ as a base provided comparable results. On the other hand, the molecular weight of **6a** lowered ($M_n = 2700$, PDI = 1.79) in the absence of Bu₄NBr as a phase-transfer catalyst.

An all-cis arrangement of vinylenes linkages was confirmed by NMR spectroscopy. Figure 1 shows the ¹H NMR spectrum of **6a** ($M_n = 2700$), together with the spectrum of (Z,Z)-2,5-dioctyloxy-4'-(2-bromoethenyl)stilbene (**7**), which was prepared as a minimum model of an all-cis PPV. As already shown by Pang et al.,^{5c} the signal at δ 3.54 is due to OCH₂ protons of octyloxy groups adjacent to (Z)-vinylenes units. On the other hand, the corresponding signal for the *trans*-PPV structure (δ 4.08) was not detected. The small signals observed at δ 3.95 (a) and 3.65 (b) with the same intensities are assignable to a 2,5-dioctyloxyphenyl group at a polymer end by comparison with the spectrum of **7**.¹⁶ Furthermore, vinylic proton signals at δ 7.00 (c) and 6.38 (d) are ascribed to the presence of a BrCH=CH group at the other end of the polymer.

All-cis PPVs thus prepared were isomerized to all-trans PPVs under photoirradiation. Figure 2A shows a change of the UV–vis spectrum of **6a** during the isomerization. When a dilute solution of all-cis **6a** ($M_n = 4700$) in benzene was irradiated

(9) DPCB-OMe = 1,2-bis(4-methoxyphenyl)-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutene; Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501.

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(15) GPC data based on polystyrene standards.

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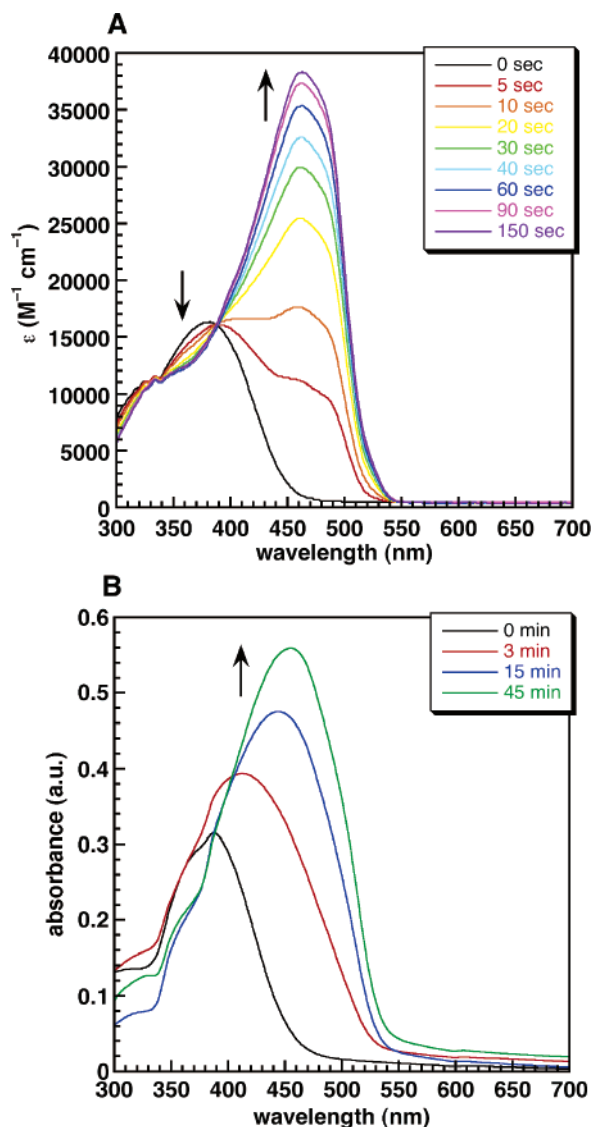


Figure 2. Changes of UV-vis absorption spectra of all-cis **6a** ($M_n = 4700$) under photoirradiation in benzene (A) and in a film (B).

with a high-pressure Xe lamp (2.1 mW cm^{-2}) at room temperature, the $\pi-\pi^*$ transition at 382 nm decreased rapidly, to be replaced with a strong absorption at 463 nm ($\epsilon = 38200 \text{ M}^{-1} \text{ cm}^{-1}$), which was almost identical to that of all-trans **6a** ($M_n = 5000$). The spectroscopic change occurred within a few minutes, maintaining isosbestic points at 334 and 388 nm. The formation of all-trans **6a** was also confirmed by ^1H NMR spectroscopy (Figure 1C).⁶ Thus, the PPV **6a** was found to undergo a clean “one-way” photoisomerization¹⁷ from the all-cis isomer to the all-trans isomer, and this behavior is in contrast to the reversible isomerization of stilbene- and azobenzene-containing polymers.¹⁸

The cis-to-trans isomerization of PPVs also took place in the solid state. A thin film of all-cis PPV **6a** (ca. 90 nm thick), which was prepared from a CHCl_3 solution by spin-coating on a quartz plate, was irradiated with strong UV light (35.5 mW cm^{-2}) at room temperature under a nitrogen

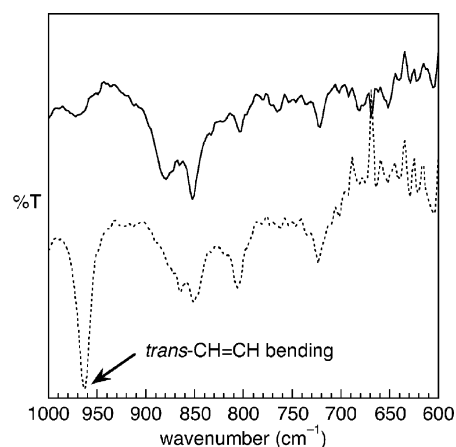


Figure 3. IR-RAS spectra of a film of all-cis **6a** before (solid line) and after (dotted line) photoirradiation.

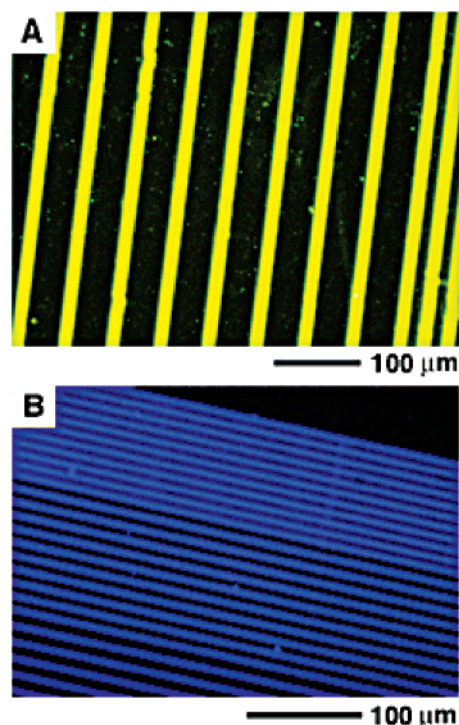


Figure 4. Fluorescent images of micropatterned **6a** (A) and **6b** (B).

atmosphere. The color of the film gradually changed from pale yellow to orange and became unchanged after 45 min (Figure 2B). The UV-vis spectrum at this stage was consistent with the formation of *trans*-PPV, and IR-RAS analysis of the film supported this conclusion (Figure 3). Interestingly, the PPV film thus prepared was much less soluble than that before irradiation. Accordingly, a very simple method for direct patterning of *trans*-PPV on a micrometer scale was developed. Thus, UV light was irradiated for 45 min through a photomask onto a film of all-cis **6a** coated on a quartz plate. The plate was rinsed with CHCl_3 to remove those parts of the PPV film that were not irradiated. Figure 4A shows an optical image of the resulting plate, which was photographed under UV light. A well-resolved pattern is observed with yellowish green emission. In a similar procedure, a micropattern with blue-light emission was developed from all-cis **6b** with *m*-phenylene units (Figure 4B).

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Conclusion

In conclusion, a highly stereocontrolled synthesis of all-cis PPVs has been successfully accomplished using the Suzuki–Miyaura-type polycondensation. (*Z,Z*)-Bis(2-bromoethenyl)-benzenes, used as starting monomers, were readily prepared by using complex **1** bearing an sp²-hybridized phosphorus ligand as a (*Z*)-selective double hydrosilylation catalyst for diethynylbenzenes. The all-cis PPVs thus prepared undergo one-way photoisomerization to the corresponding PPVs with (*E*)-vinylene linkages under photoirradiation. This property is applicable to direct patterning of PPVs on a micrometer scale. The method is extremely simple and should be useful for constructing functional materials used in optoelectronics.^{19,20}

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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